CALORIMETRIC DETERMINATION OF THE HEAT OF SOLUTION OF CALCIUM IN LIQUID AMMONIA AND THE HEAT OF REACTION OF CALCIUM WITH THE AMMONIUM ION IN LIQUID AMMONIA

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Calorimetric determination of the heat of solution of calcium in liquid ammonia and the heat of reaction of calcium with the ammonium ion in liquid ammonia.

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Thesis

CALORIMETRIC DETERMINATION OF THE HEAT OF SOLUTION OF CALCIUM IN LIQUID AMMONIA AND THE HEAT OF REACTION OF CALCIUM WITH THE AMMONIUM ION IN LIQUID AMMONIA

by

SUMNER P. WOLSKY
(B.S., Northeastern Univ., 1947)

Submitted in partial fulfillment of the
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OUTLINE

CALORIMETRIC DETERMINATION OF THE HEAT OF SOLUTION OF CALCIUM IN LIQUID AMMONIA AND THE HEAT OF REACTION OF CALCIUM WITH THE AMMONIUM ION IN LIQUID AMMONIA

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CALORIMETRIC DETERMINATION OF THE HEAT OF SOLUTION OF CALCIUM IN LIQUID AMMONIA AND THE HEAT OF REACTION OF CALCIUM WITH AMMONIUM ION IN LIQUID AMMONIA

The liquid ammonia solutions of the alkali metals present a deep blue color when dilute and a bronze-like appearance when concentrated. These solutions have been found to be characterized by certain anomalous properties which are generally similar for this series of metals. Vapor pressure measurements[1] have indicated the apparent molecular weight of sodium dissolved in liquid ammonia to be at least as low as 23, and in sufficiently dilute solutions to be lower because of dissociation. The similarity of ammonia solutions of alkali metals is most markedly demonstrated by absorption spectra and conductivity measurements. Gibson and Argo[2] found the absorption spectra of dilute solutions of lithium, sodium, and potassium in liquid ammonia to be identical. In 1921 Kraus[3] observed that the conductance of ammonia solutions of lithium, sodium, and potassium varied from metallic to electrolytic, and that there was a marked similarity of the curves obtained when the conductances of these solutions were plotted.

1. C.A. Kraus, J. Am. Chem. Soc. 30, 1197 (1908)
2. Gibson and Argo , ibid 40, 1327 (1918)
3. C.A. Kraus, ibid 43, 749 (1921)

To explain the unique properties of these solutions Kraus[4] proposed the following equilibria:

$$M \rightleftharpoons M^{+} + e^{-} \qquad e^{-} + xNH_3 \rightleftharpoons e^{-}_{(xNH_3)}$$

in which the solution of the metal is accompanied by partial ionization of the atom into electrons and positive ions which in turn are solvated by the solvent molecules. The absorption work of Gibson and Argo[2] lent further support to the theory that the similarity of the alkali metal solutions is due to the solvated electron.

The concentration dependence of the paramagnetism of alkali metal solutions in liquid ammonia observed in recent studies[5,6] of the magnetic properties of these solutions has caused modification of the original Kraus theory. On the basis of complete ionization of the metal (Kraus proposed only partial ionization), the F-F' center equilibrium

$$e^{-}\downarrow\uparrow e^{-} \rightleftharpoons e^{-}\downarrow + e^{-}\uparrow$$

has been proposed by Freed and Sugarman[6] and developed further by Ogg[7]. The left side of this equilibrium indicates the pairing of electrons in the solution, while the right side

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4. C.A. Kraus, J. Am. Chem. Soc. 30, 1323 (1908)
5. (a) Huster, Ann. Physik 33, 477 (1938)
   (b) Freed and Thode, Nature 134, 774 (1934)
6. Freed and Sugarman, J. Chem. Physics 11, 354(1943)
7. Ogg, J. Am. Chem. Soc. 68, 155 (1946)

indicates unpaired electrons. An alternative proposal for accounting for the concentration dependence of the paramagnetism of these solutions has been offered by Huster[5b] in which we have the diatomic molecules containing the paired electrons in the form of a covalent bond.

$$M_{2(NH_3)} \rightleftharpoons 2\,M^{+}_{(NH_3)} + 2e^{-}_{(NH_3)}$$

Since in both the old postulates and the more recent modifications the theoretical nature of the dilute solutions, aside from the positive ion, remains the same, namely the solvated electron, and since this has been confirmed by experimental evidence, we may expect that the properties of ammonia solutions dependent upon the solvated electron will be the same for all the alkali metals. Recent thermochemical studies[8,9] of the dilute solutions of lithium, sodium, potassium, and cesium have strengthened this view since it has been found that all these solutions possess a similar heat of reaction in liquid ammonia with the ammonium ion ($\Delta H = 40{,}300 \pm 1000$ calories per gram atom of metal). This value was obtained by subtracting (a) the heat effect associated with the solution of the metal in liquid ammonia

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[8] L.V. Coulter, Unpublished research

[9] R.H. Maybury, Calorimetric Determination of the Heats of Reaction of Lithium and Cesium with the Ammonium Ion in Liquid Ammonia (unpublished Master's thesis, Boston University, Boston, 1948)

at infinite dilution

$$M \rightarrow M^{+}_{(NH_3)} + e^{-}_{(NH_3)} \qquad \Delta H_1$$

from (b) the heat effect associated with the reaction of the solid metal with the ammonium ion in liquid ammonia

$$M + NH^{+}_{4(NH_3)} \rightarrow M^{+}_{(NH_3)} + NH_{3(l)} + \tfrac{1}{2} H_{2(g)} \qquad \Delta H_2$$

In Table 1 average values of ΔH_2 for each of the metals lithium, sodium, potassium, and cesium have been combined with heat of solution values, ΔH_1, obtained from the literature.

TABLE 1

Reactants	Average Heat of Reaction/gm-atom	Heat of Solution/ gm-atom	$\Delta H_3 = \Delta H_2 - \Delta H_1$
$Li + NH_4Br$	-50,200[9] cal.	-9,600[9] cal.	-40,600 cal.
$Na + NH_4Br$	-38,400[8]	1,400[10]	-39,800
$Na + NH_4Cl$	-38,700[8]	1,400[10]	-40,100
$K + NH_4Br$	-39,700[8]	0[11]	-39,700
$Cs + NH_4Br$	-41,400[9]	0[11]	-41,400
		Mean	40,300 1000 cal.

The ΔH_3 values obtained agree with the mean of 40,300 calories well within experimental error. One is led, therefore, to the conclusion that the heat of reaction of sodium, lithium, potassium, and cesium solutions in liquid ammonia with ammonium

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[10] Kraus and Schmidt, J. Am. Chem. Soc. 56, 2298(1934)
[11] Schmidt, Studer, and Sottysiak, J. Am. Chem. Soc. 60, 2780 (1938)

ion is independent of the alkali metal used in the reaction, and that it may be presumed to be due to the common reaction between the solvated electron and the ammonium ion as follows:

$$NH_{4(NH_3)}^{+} + e^{-}_{(NH_3)} = NH_{3(l)} + \tfrac{1}{2}H_{2\ (g)}$$

Extension of this concept of solutions to the alkaline earth metals would lead one to expect properties of a similar nature when compared on a proper concentration basis since twice the number of electrons are involved per atom.

The alkaline earth metals dissolve in liquid ammonia to form solutions similar in appearance to the alkali metal solutions, the dilute solution being deep blue in color, and the concentrated solution presenting a bronze-metallic appearance. Study of phase diagrams has revealed the formation of the ammoniates $Ca(NH_3)_6$[12], $Ba(NH3)_6$, and $Sr(NH_3)_6$. Recently the formation of the calcium, barium, and strontium ammoniates was confirmed by Birch and MacDonald[13] who also claimed discovery of the ammoniate $Li(NH_3)_4$, however further work is necessary to verify this latter point, since in the past[12] it has been found that upon distillation of the alkali metal solutions the residue consisted only of the original metal.

As stated previously, extension of the concept of solutions, as indicated by studies of the dilute solutions of

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12. Kraus and Johnson, J. Am. Chem. Soc. 47, 725 (1925)
13. Birch and MacDonald, Trans. Faraday Soc. 43, 792(1947)

alkali metals in liquid ammonia solutions,to the alkaline earth metals might lead one to expect similar properties. The validity of this expectancy, however, may be questioned when various studies of the solutions of alkaline earth metals in liquid ammonia are considered.

Gibson and Argo[2] observed that the absorption spectrum of dilute solutions of calcium in liquid ammonia differed from that obtained for the alkali metal solutions. It can be noted from Gibson and Argo's plot of the wavelength (λ) against the logarithm of the extinction coefficient[14] (ε) (Figure 1) that calcium not only does not give a straight line as in the case of lithium, sodium, potassium, and magnesium, but that calcium solutions show indications of increased absorption at the longer wavelengths. Unfortunately only a single measurement was made on calcium solutions, and the authors were unable to verify this behavior. However it was remarked that this deviation may have been due to the impurities present in the calcium. (The following analysis is given of the calcium: 97.75% Ca, 0.85% Cl, 1.08% Fe_2O_3 and Al_2O_3, and trace of Mg.) The basis for this suposition arises from studies of the absorption spectrum of sodium in methylamine where it was found that the absorption spectrum was markedly affected by the presence of impurities. Therefore it seems very possible that

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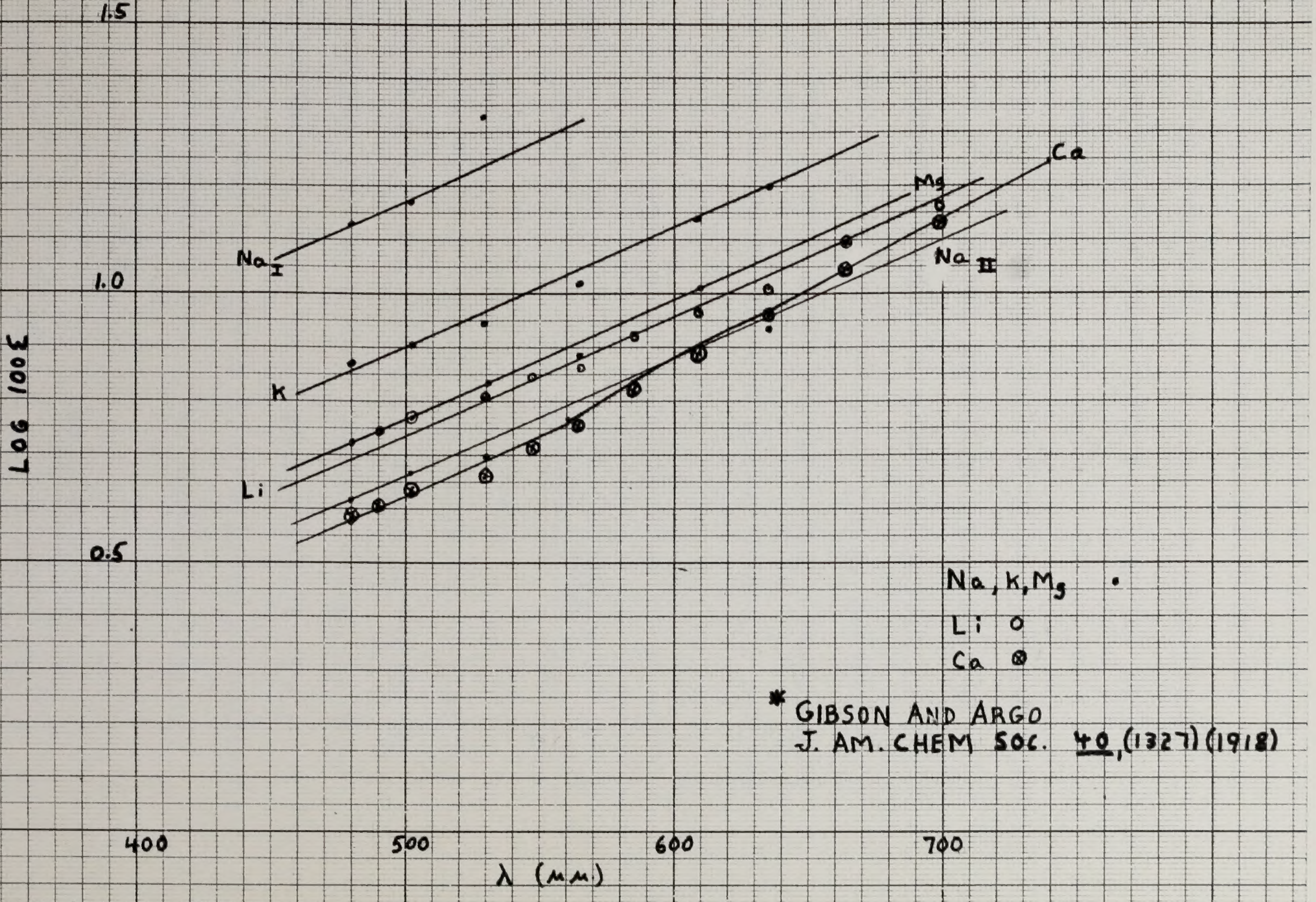
[14] $\varepsilon = -(\log I/I_0)/d$ where I_0 is the initial intensity of the light and I is the intensity after passing d centimeters of the absorbing medium.

FIGURE 1
THE ABSORPTION SPECTRA OF Na, Li, K, Mg, Ca IN LIQUID AMMONIA*



* GIBSON AND ARGO
J. AM. CHEM SOC. 40, (1327) (1918)

the absorption spectrum of a dilute solution of calcium in liquid ammonia might have been affected similarly by the presence of impurities, and that the absorption spectrum of pure calcium would not differ from those for lithium, sodium, potassium, and magnesium.

The molal magnetic susceptibilities of calcium and barium have been determined[6], and it has been found that whereas dilute solutions of barium possess a molal suceptibility expected for ionization into two electrons per gram-atom, calcium solutions have a much lower suceptibility. For example at -33°C we have the following susceptibility data for calcium and barium.

TABLE 2

Calcium		Barium	
Normality	$\lambda_m \times 10^{-6}$	Normality	$\lambda_m \times 10^{-6}$
0.00489	1140	0.00206	2280

Here the molal susceptibility (λ_m) of barium is twice that for calcium. In accounting for this Freed and Sugarman[6] point to the case of sodium and potassium where sodium, a smaller atom than potassium, exhibits a lower molal susceptibility than potassium. As can be seen from Table 3, at a given concentration the susceptibility of sodium is less than that of potassium.

TABLE 3[15]

at 0.02 n	at 0.01 n
sodium $\lambda_m = 400 \times 10^{-6}$	sodium $\lambda_m = 650 \times 10^{-6}$
potassium $\lambda_m = 550 \times 10^{-6}$	potassium $\lambda_m = 825 \times 10^{-6}$

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[15] Yost and Russell, Systematic Inorganic Chemistry, Prentice Hall, N.Y. (1944)

Similarly one would expect calcium, a smaller atom than barium, to exhibit a lower susceptibility than barium. Therefore the greater interaction of the smaller calcium ion with its environment is at least one probable contributing factor to the lower susceptibility value.

Yost and Russell[15] have offered another explanation of this apparent anomaly in the magnetic properties of dilute solutions of calcium in liquid ammonia, accounting for it on the basis of ionization of only one electron per calcium ion giving Ca^{+} which would occur coupled as Ca$_2^{++}$. Thus the paramagnetism associated with the Ca^{+} ion would be eliminated. That such a system probably exists in saturated solutions is indicated by density measurements.[16] At -35°C and at a concentration of 7 moles ammonia/calcium (sat.) the density was found to be 0.651. This saturated solution also yielded a volume expansion of 44 cc. per gram atom of calcium. Since sodium when dissolved in liquid ammonia yields an expansion of 43 cc., and since the atomic and ionic radii of sodium and calcium are very similar, it appears likely that in saturated solutions of calcium, as in the solution of sodium, there is only ionization of one elctron per gram-atom of metal used. These density measurements, however, do not apply to dilute solutions.

The problem of one or two electron ionization of calcium

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16. L.V. Coulter, *Northwest Science* (1942)

may be approached thermochemically. Since recent work on alkali metal solutions [8,9] has shown these solutions all to possess a similar heat of reaction with ammonium ion in liquid ammonia, it is possible to use this value as a means of comparing calcium solutions. On this basis there are three possible reactions of the solvated electron and the ammonium ion, each with a different heat effect associated with it. For one electron ionization to form Ca_2^{++} there exists two possible reactions:

$$(1)\ \tfrac{1}{2}(Ca_2^{++})_{(NH_3)} + e^-_{(NH_3)} + NH^+_{4(NH_3)} = NH_{3\,(l)} + \tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}(Ca_2^{++})_{(NH_3)}$$

In this reaction Ca^+ in the form Ca_2^{++} is not involved in the reaction. The reaction therefore being completely analogous to that of the alkali metals would be expected to yield a similar heat effect of 40,300 calories per gram-atom of calcium.

$$(2)\ \tfrac{1}{2}Ca^{++}_{2(NH_3)} + e^-_{(NH_3)} + 2NH^+_{4(NH_3)} = Ca^{++}_{(NH_3)} + 2NH_3(l) + H_{2(g)}$$

In this second possible reaction involving one electron ionization there would be energy absorbed in the uncoupling of Ca_2^{++} and in the ionization of Ca^+ to Ca^{++}. The total energy absorbed due to these two effects would be greater than the energy gained from the solvation of the electron, therefore the heat effect expected would be larger than in the above case, but it would probably be less than 80,600 calories (2 x 40,300). For two electron ionization of the calcium atom we would have the following reaction:

$$(3)\ Ca^{++}_{(NH_3)} + 2e^{-}_{(NH_3)} + 2NH^{+}_{4(NH_3)} = 2NH_{3(l)} + H_{2(g)} + Ca^{++}_{(NH_3)}$$

which would yield a heat effect of 2 x 40,300 calories or 80,600 calories/gram-atom. Ca^{++} does not participate in this reaction but it is included in the equation to show the nature of the ionization.

Direct determination of the heat effect associated with the above reaction is not experimentally feasible. It can be seen that the experimental difficulties involved in the mixing of two solutions of relatively large volumes under controlled conditions so as to prevent a sudden, almost instantaneous, evolution of heat are indeed great. Fortunately indirect determination by the combination of the heat effects of two easily studied reactions has proved possible and also experimentally simpler.[8,9] Therefore this method has been employed in this research.

Assuming first one electron ionization we have the following equation for the solution of calcium in liquid ammonia:

$$(a)\quad Ca \longrightarrow \tfrac{1}{2}Ca^{++}_{2(NH_3)} + e^{-}_{(NH_3)} \qquad \Delta H_1$$

where ΔH_1 is the heat effect associated with the reaction. The solid calcium metal reacts with ammonium ion in liquid ammonia as follows:

$$(b)\ Ca_{(s)} + 2NH^{+}_{4(NH_3)} = Ca^{++}_{(NH_3)} + 2NH_{3(l)} + H_{2(g)} \qquad \Delta H_2$$

where the heat effect associated with this reaction is ΔH_2. By combining these reactions in the following manner we get the

$$(a)\quad Ca \longrightarrow \tfrac{1}{2}Ca_{2\,(NH_3)}^{++} + e^{-}_{(NH_3)} \qquad \Delta H_1$$

$$(b)\quad Ca_{(s)} + 2NH_{4\,(NH_3)}^{+} \longrightarrow Ca_{(NH_3)}^{++} + 2\,NH_{3(l)} + H_{2(g)} \qquad \Delta H_2$$

$$(2)\quad \tfrac{1}{2}Ca_{2\,(NH_3)}^{++} + 2NH_{4\,(NH_3)}^{+} + e^{-}_{(NH_3)} \longrightarrow Ca_{(NH_3)}^{++} + 2NH_{3(l)} + H_{2(g)}$$

$$\Delta H_3 = \Delta H_2 - \Delta H_1$$

desired reaction (2) where ΔH_3 is the heat effect associated with the oxidation of calcium, in solution with ammonium ion.

Similarly we may arrive at ΔH_3 for reactions (1) and (3).

$$(a)\quad Ca \longrightarrow \tfrac{1}{2}Ca_{2\,(NH_3)}^{++} + e^{-}_{(NH_3)} \qquad \Delta H_1$$

$$(b)\quad Ca_{(s)} + NH_{4\,(NH_3)}^{+} \longrightarrow \tfrac{1}{2}Ca_{2\,(NH_3)}^{++} + \tfrac{1}{2}H_{2(g)} + NH_{3(l)} \qquad \Delta H_2$$

$$(1)\quad \tfrac{1}{2}(Ca_2^{++})_{(NH_3)} + e^{-}_{(NH_3)} + NH_{4\,(NH_3)}^{+} \longrightarrow NH_{3(l)} + \tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}(Ca_2^{++})_{(NH_3)}$$

$$\Delta H_3 = \Delta H_2 - \Delta H_1$$

$$(a)\quad Ca \longrightarrow Ca_{(NH_3)}^{++} + 2e^{-}_{(NH_3)} \qquad \Delta H_1$$

$$(b)\quad Ca_{(s)} + 2NH_{4\,(NH_3)}^{+} \longrightarrow Ca_{(NH_3)}^{++} + H_{2(g)} + 2NH_{3(l)} \qquad \Delta H_2$$

$$(3)\quad Ca_{(NH_3)}^{++} + 2e^{-}_{(NH_3)} + 2NH_{4\,(NH_3)}^{+} \longrightarrow 2NH_{3(l)} + H_{2(g)} + Ca_{(NH_3)}^{++}$$

$$\Delta H_3 = \Delta H_2 - \Delta H_1$$

It is the purpose of this research to determine the heat effects ΔH_1 and ΔH_2 at infinite dilution, and by their combination to arrive at the value for ΔH_3. Then by comparison of ΔH_3 with the ΔH_3 of the three possible theoretical

reactions of the solvated electron with ammonium ion in calcium solutions as mentioned previously, it should be possible to determine the nature of the ionization of calcium in liquid ammonia.

The heat of solution of calcium in liquid ammonia has been determined by Schmidt[17] but over only a short concentration range with the most dilute measurements corresponding to a little more than 200 moles of ammonia per mole of calcium. At the dilutions studied the heat of solution is still changing rapidly with concentration indicating the necessity for performing this research at much higher dilutions.

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17. Schmidt, Studer, and Sottysiak, J. Am. Chem. Soc. 60, 2780 (1938)

II. EXPERIMENTAL

The method and apparatus employed in this research was identical, except for a few minor changes, with that used by R. Maybury[9] in his determination of the heats of reaction of lithium and cesium in liquid ammonia.

The heat of solution or reaction can be represented as the sum of the heat effects accompanying (1) the temperature change of the calorimeter and its contents, and (2) the vaporization of ammonia.

The first of these heat effects can be evaluated by determining potentiometrically the temperature change incurred during the reaction by a system of known total heat capacity. The second of these effects is determined by measurement of the gases vaporized and collected during the reaction.

Special techniques for making thermochemical measurements in liquid ammonia were first developed by Kraus[18] and Schmidt[19]. R. Maybury[9], in his thesis work, used a modified version of the Schmidt apparatus. It was with the modified calorimetric apparatus (Figure 2) that this research was conducted with changes being made only in the construction

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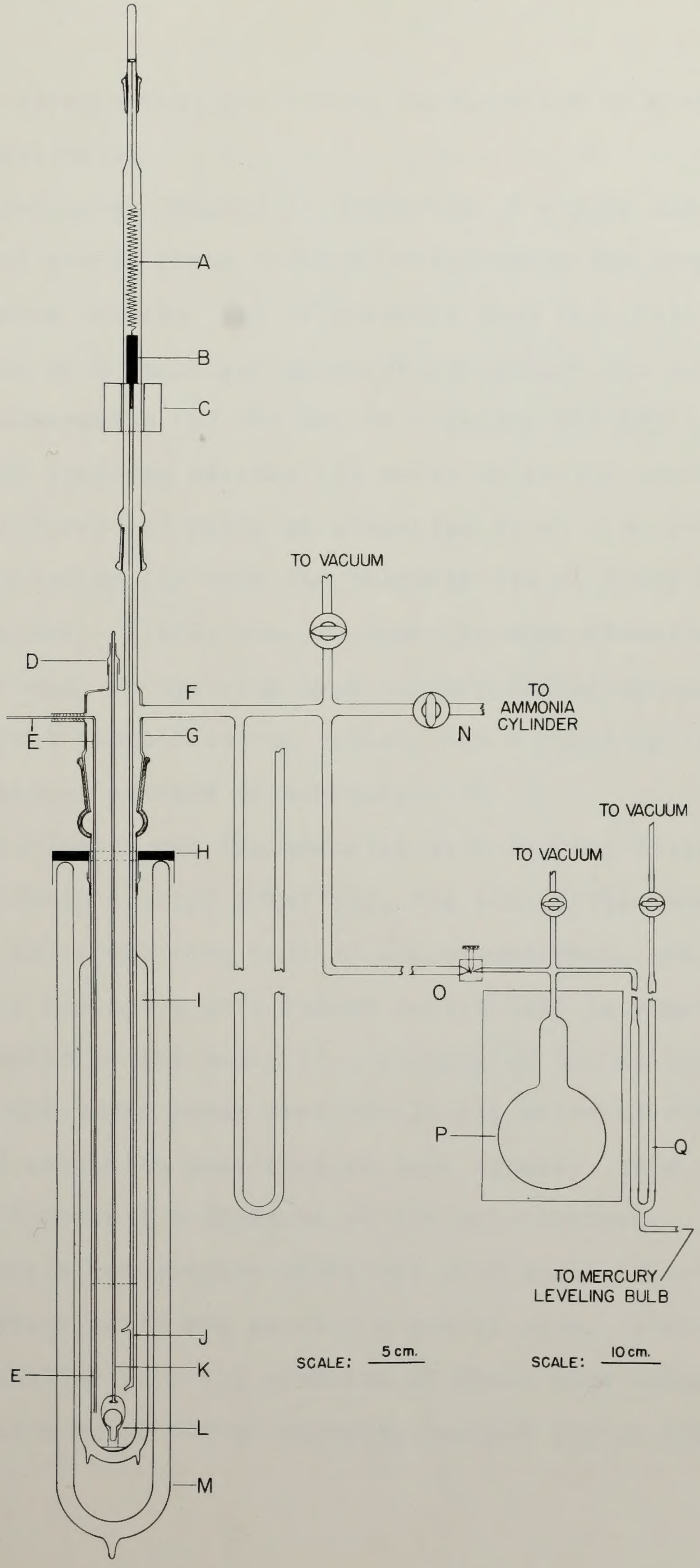
[18] C.A. Kraus and J. Ridderhof, J. Am. Chem. Soc. 56, 79 (1934)
Kraus and Prescott, ibid 56, 86 (1934)
Kraus and Schmidt, ibid 56, 2297 (1934)

[19] Schmidt, Sottysiak, and Kluge, J. Am. Chem. Soc. 56, 2509 (1936)

FIG. 2


A
B
C
TO VACUUM
D
F
TO AMMONIA CYLINDER
E
G
N
TO VACUUM
H
TO VACUUM
I
O
P
Q
TO MERCURY LEVELING BULB
J
SCALE: 5 cm.
SCALE: 10 cm.
E
K
L
M

of the current interrupter, and in the installation of a more sensitive potentiometer.

The calorimeter (Figure 2) consisted of a long Dewar (I) with a taper ground glass joint a little above the ring seal of the vacuum jacket. The calorimeter head (G), held tightly in place by a small spring stretched across the top, carried the thermocouple (E) the sample crushing rod (D) connected to the platinum stirrup (L) which holds the sample bulb, and the stirrer (J) which is connected to an iron bob (B) and thence to a spring (A) with the solenoid (C) slipping down around the iron bob. A side arm (F) from the head connected the calorimeter with an open-end type mercury filled manometer, a vacuum pump, the gas-collecting system, and a small cylinder containing a weighed ammount of ammonia.

The calorimeter was thermostated with boiling liquid ammonia contained in a large Dewar (M), the lip of the Dewar being a little above the ring seal of the calorimeter, and pressing tightly against a soft rubber gasket held in a metal collar (H) attached to the unjacketed portion of the calorimeter. Both the inner and outer Dewar were completely silvered except for two aligned strips on each side of both Dewars. This enabled one to observe the contents of the calorimeter.

The circuit interrupter consisted of a small induction-type motor on whose shaft was mounted a set of cams. Circuit interruption resulted from the rotation of these cams intermittently touching metal strips carrying contact points thereby

making and breaking the circuit. The number of times per minute that the circuit was opened and closed was determined by the construction of the cams. In this research the cams were made so that a stirring rate of 60 strokes per minute was maintained.

The gas-collecting system was connected to the calorimeter through the needle valve (O). This valve was used to control the rate at which the gases were drawn off from the calorimeter. The evacuated glass vessel (P), used to collect the gases evolved, had a volume of 6715 milliliters, and was immersed in a large water bath maintained at $25 \pm .1^{\circ}C$. A closed-type mannometer (Q) was used to read directly the volume of ammonia collected.

In this research the electrical measuring equipment had been improved by the use of the more sensitive White Single Potentiometer (L and N #7620 and #7621). A meter scale suspended nine feet from the floor and seventeen feet from the galvonometer was reflected by the mirror of the galvonometer into a 15 power telescope giving a sensitivity of approximately 5.1 scale divisions per microvolt.

Two 2 volt batteries were connected to the potentiometer through a closed circuit thereby providing an even discharge rate.

Experimental Procedure

A typical experimental determination of either ΔH_1 or ΔH_2 required several necessary preparations including prepa-

ration of the sample, purification of the ammonium salt, assembly of the calorimeter, and checking of the electrical measuring equipment. This was followed by distillation of the ammonia into the calorimeter, time-temperature measurements at one minute intervals made prior to, during, and after the reaction period, and finally the determination of the volume of gas evolved.

Preparation of the Sample

The sample bulbs used in these experiments were made by rapidly fusing together the end of 6mm. O.D. pyrex tubing in an oxygen-gas flame, and then blowing out into a bulb of about 1-2 ml. volume. The bulbs had to be made so as to just bend slight pressure of a pencil point and yet be able to hold a vacuum.

The stem was cut off at a length of 6 cm. and the end firepolished. The volume of the bulb was determined to 0.01 milliliters. The bulb was cleaned, dried, and weighed to the nearest 0.1 milligram along with a short piece of glass rod which filled the stem section of the bulb. Experience had dictated the necessity for using the solid glass rod lest in the reaction some of the unreacted sample become lodged in the stem of the bulb.

The calcium used was moulded in cylindrical bars by the Metal Hydrides Co. and gave the following spectrographic analysis: sodium 10 ppm, lithium 10 ppm., barium 1-2 ppm.,

lead 50-100 ppm., magnesium 100 ppm., tin - , boron 2 ppm., silicon 20 ppm., iron 10 ppm., manganese 10 ppm., and aluminum 50 ppm.. The bars of calcium were kept under mineral oil to prevent the formation of oxides and nitrides.

The dimensions (diameter and length) necessary to give a cylinder of calcium of the desired weight were calculated using a density of 1.54 grams/cc. A sample calculation is as follows:

> A 0.154 gram sample is desired therefore the total volume of the sample is 0.154 g./1.54 g./cc. equals 0.100 cc. equals 100 mm^3. Then setting this volume equal to $\pi r^2 h$- the volume of a cylinder - and arbitrarily taking $r = 2$ mm. (the sample will have a diameter of 4 mm.) we get :
>
> $$100\ mm^3 = 3.14 \times 4\ mm^2 \times h$$
> $$h = 7.96\ mm.$$

Thus to get a sample of calcium weighing 0.154 grams a cylinder 4 mm. in diameter and 7.96 mm. long had to be cut.

The moulded bars were turned on a lathe to the calculated diameter, cut off at the desired length, and immediately placed in a beaker of heavy mineral oil. It was necessary to do all turning of calcium metal under heavy mineral oil, first, to prevent excessive heating and the possibility of fire, and second, to insure that the final sample would have a bright metallic surface free from oxides and nitrides. Experiments showed that the metallic surface would not darken perceptibly for at least one hour when kept under heavy mineral oil which was freshly poured from a tightly capped bottle.

The sample was removed from the oil, rapidly transferred through a series of three dried benzene washes, and introduced into a sample bulb that had previously been filled with dry benzene. The solid glass rod was inserted in the stem, and directed the sample into the bulb. The bulb was attached to a piece of rubber tubing connected to a vacuum pump through a dry ice-trichloroethylene trap. The benzene was pumped off and the bulb evacuated. By playing a fine oxygen-gas flame on the lower end of the stem the glass tubing was made to collapse onto the solid rod sealing the bulb at that point. The bulb was cleaned, weighed, and the stem drawn off 1-2 cm. from the bulb. The sample bulb was now ready for use.

Preparation of the Ammonium Salt

In the reaction of calcium with an ammonium halide care had to be taken that the resulting calcium halide was soluble in liquid ammonia. On consulting solubility data it was found that only calcium iodide was soluble at the required dilutions. Ammonium iodide was therefore chosen as the ammonium salt to be reacted with the metallic calcium in liquid ammonia. The ammonium iodide was prepared by recrystallization of the C.P. grade salt from hot water. It was dried under vacuum at room temperature and placed in a vacuum dessicator. Starch-Iodide tests detected no signs of free iodine in the prepared ammonium iodide. Further tests showed that even after 1½ hours of standing in air the recrystallized ammonium iodide showed no signs of free iodine.

Advance Preparations and Assembly of the Calorimeter for a Heat of Reaction Determination

The advance preparations, the assembly of the calorimeter, and the actual procedure for making a calorimetric determination of a heat of reaction are described in great detail in the thesis of R. Maybury.[9]

Liquid ammonia purchased from the Matheson Co. and analyzed by them to be 99.7% ammonia with 0.1% nitrogen and 0.2% moisture as impurities was condensed into a medium sized cylinder containing sodium. The dried ammonia was used to fill a smaller cylinder to the desired weight.

The calorimeter was cleaned and dried, and finally the electrical measuring apparatus was checked.

The sample bulb was placed securely in the platinum stirrup directly in line with the sample crushing rod. No platinum gauze, such as was necessary in the work with lithium and cesium, was used with calcium, the reaction rate being much slower than that of lithium and cesium. A calculated amount of ammonium iodide was introduced into the calorimeter, and the sample crushing rod placed slightly above the bulb. The calorimeter head was connected to the gas-collecting system by sealing the glass line between them. The system was evacuated several times to seat the calorimeter head, and any strains produced were removed by heating with an oxygen-gas flame. The system was tested for leaks, and then evacuated. Nitrogen was run into the calorimeter through two drying tubes containing phosphorous pentoxide. This placed the ammonium

iodide in an inert atmosphere of dry nitrogen, and completed the assembling of the apparatus. The time elapsed between the removal of the ammonium iodide from the vacuum dessicator was not greater than one hour.

The Procedure for Making a Calorimetric Determination of the Heat of Reaction of Calcium Metal with Ammonium Ion

The calorimetric system was evacuated and once again checked for leaks. Dry liquid ammonia was distilled into the calorimeter from the previously prepared small cylinder. The distillation was facilitated by surrounding the inner Dewar with a dry ice-trichloroethylene mixture contained in the large outer Dewar. When the manometer pressure indicated complete distillation, stopcock N (Figure 2) was closed, and the small ammonia cylinder detached and weighed to determine the amount of ammonia in the calorimeter. All necessary connections having been made (connection of one inlet tube to allow the ammonia to run into the Dewar, and one to allow ammonia vapors to bubble through the ammonia) the Dewar was forced tightly against the rubber gasket with wooden blocks, and fastened to the metal collar with friction tape. Liquid ammonia was run into the Dewar through an inlet tube not indicated in Figure 2.

When the outer Dewar was filled just below the ring seal, the inlets were switched, and the ammonia supply adjusted so as to bring about gentle bubbling through the liquid. The current interrupter was started to provide a constant stirring of the contents of the calorimeter.

To adjust the temperature of the calorimeter near that of

the thermostating bath of liquid ammonia the needle valve was opened, and some of the vapors allowed to flow into the previously evacuated gas-collecting system.

The pressure of ammonia in the gas-collecting system was read directly from the mannometer connected to the gas-collecting vessel. A leveling bulb was used to lower the mercury level to a reference mark within the enlarged portion of the manometer arm. The volume of the gas-collecting system having been calibrated with the mercury in the left arm of the manometer at this point, all pressure readings must therefore be taken with the mercury at this calibration mark.

The temperature of the water bath surrounding the gas-collecting flask was maintained at 25 ± .1°C during the pressure readings.

The gas-collecting system was again evacuated in preparation for the breaking of the sample bulb.

While the calorimeter and its contents were approaching temperature equilibrium, the thermocouple circuit was prepared. The thermocouple reference junction, prepared from distilled water ice, was put in place, and the knife switch connecting the thermocouple to the potentiometer was closed. The battery circuit of the potentiometer was balanced against a standard cell.

The temperatures were observed as scale readings of the galvanometer for respective potentiometer settings. When the temperature of the calorimeter approached the theoretically

expected equilibrium temperature, calculated using the barometric pressure, potentiometric and line pressure readings were begun.

The temperature readings were taken at one minute intervals during a period preceding the reaction, during the reaction period, and through a period following the reaction. Line pressure readings were taken every five- ten minutes.

When the rate of change of the temperature of the calorimeter and when the line pressure had attained constant values over a one half hour period, the reaction was initiated. A short thrust of the sample crushing rod fractured the thin walled sample bulb. Vigorous bubbling of the solution due to the evolution of hydrogen and ammonia was observed. The line pressure was maintained constant by carefully withdrawing the vaporized gases through the needle valve into the gas-collecting system. During the reaction period, which may be from five to thirty minutes, potentiometer readings were taken at the usual one minute interval. When the reaction was over the needle valve was closed and scale readings recorded until the temperature again had assumed a constant rate of change. Line pressure readings were taken at frequent intervals during this period. Upon completion of temperature readings the pressure of the collected gases was measured at the calibration mark using a Gaertner Cathetometer. The liquid level of the ammonia solution and a reference mark were similarly determined.

similarly determined.

The experimental procedure involved in a heat of solution determination was only very slightly modified. The platinum stirrup was not used, but instead the stem of the sample bulb was sealed to the sample rod. The bulb was then fractured, as before, by thrusting downward on the sample rod. Also, in heat of solution determinations no ammonium salt was dissolved in the liquid ammonia, and therefore it was unnecessary to have an inert atmosphere of dry nitrogen in the calorimeter prior to the experiment.

Heat capacity measurements (see Appendix) were made in a manner similar to the determination of the heat of reaction of calcium metal in liquid ammonia.

After some of the experiments a determination was made of the weight of calcium actually in the calorimeter. This was done in the following manner.

When the final cathetometer readings had been taken, the system was opened to the air, and the ammonia allowed to evaporate. The glass line connection between the calorimeter head and the gas-collecting system was then broken. The calorimeter head was lifted out of the ground glass joint and clamped in position so that those areas of the thermocouple, stirrer, sample crushing rod, and stirrup (still containing the remnants of the sample bulb) which were immersed in the liquid ammonia during the experiment remained in the calorimeter. A fine stream of distilled water was played on the

calorimeter walls and on the thermocouple, stirrer, sample rod, and stirrup. In this manner the calcium salt left on the glassware was dissolved and the washings collected in the bottom of the calorimeter. After having thoroughly washed the thermocouple, stirrer, sample rod, and stirrup, the calorimeter head was removed completely from the calorimeter. The washings collected in the calorimeter were removed with a pipette and placed in a beaker. The walls of the calorimeter were washed several times with distilled water till all the calcium had been dissolved. A very slightly acid solution sometimes facilitated this procedure.

The washings were made very slightly acid to insure that all the calcium was dissolved. The solution was filtered to remove any glass fragments due to the crushing of the sample bulb, and then diluted with distilled water in a one liter volumetric flask. Two aliquots of 300 ml. each were taken to be used in the determination of calcium as calcium oxalate.[20]

Five milliters of hydrochloric acid were added to each aliquot. A solution of three grams of ammonium oxalate dissolved in 50 ml. of distilled water was added to the acid solution. Using methyl red as an indicator, the solution was

[20] Kolthoff and Sandell, Textbook of Quantitative Inorganic Analysis, The MacMillan Co., New York, 1936

made slightly basic with 1:1 ammonium hydroxide, and then allowed to stand for one hour. The precipitate of calcium oxalate formed was filtered through a sintered glass filter, washed with 1% ammonium oxalate solution, and finally washed with several portions of cold distilled water. The precipitate was dissolved on the filter with 50 ml. of 1:8 sulfuric acid. The acid solution of the oxalate was diluted to a concentration of 1-1.5N and heated to 80°C. The warm acid solution was then titrated using potassium permanganate which had been standardized against sodium oxalate.

The weight of calcium present was determined from the normality and volume of the permanganate used.

III. PRESENTATION OF THE DATA

The experimental data recorded in each experiment is presented in Tables 4-16.

A. The Weight of the Calcium Sample

The weight of the calcium sample was determined from the weight of the sealed bulb containing the calcium and the weight of the empty bulb. The volume of the bulb was necessary to determine the weight of calcium in vacuo.

Wt. in vacuo = wt. obs. + vol. of bulb x 0.00118

B. The Weight of Ammonia in the Calorimeter

The small cylinder containing the dried ammonia was weighed prior to and after the distillation of the ammonia into the calorimeter. In this manner the weight of ammonia transferred to the calorimeter was obtained. The amount of ammonia that fills the calorimeter line as vapor was calculated from the known volume of the line and the pressure reading indicated by the manometer. This value (0.84 grams for this research) subtracted from the weight of ammonia distilled into the calorimeter yielded the weight of ammonia actually in the calorimeter.

C. The Weight of Ammonium Iodide Used

Two moles of ammonium iodide were required for each gram-atom of calcium metal used in the reaction. A ten percent excess of the theoretical amount of ammonium salt necessary was used.

D. Liquid Height in Calorimeter

Cathetometer readings of the liquid meniscus and of a reference were recorded. The liquid height from the bottom of the calorimeter was calculated from the known distance of the reference mark from the inside bottom of the calorimeter (176.7 mm.).

E. Analysis of the Calorimeter Contents

The contents of the calorimeter, after an experimental determination, were dissolved in water and the calcium precipitated as calcium oxalate. The volume of potassium permanganate necessary to titrate a 300 ml. aliquot of an acid solution of the oxalate was recorded. The weight of calcium present in the calorimeter, determined from the analysis, was also recorded.

F. E.M.F. Measurements

The potentiometer and galvanometer scale readings were observed for each minute interval. Any notes necessary for calculation and interpretation of the data were recorded. This included the gas-collecting system data, calorimeter line pressure readings, the exact time of the breaking of the bulb, and information concerning the reaction.

TABLE 4

EXPERIMENTAL DATA

EXPERIMENT A
DATE August 17, 1948
Determination of
Heat of Solution of
CALCIUM WITH LIQUID
AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	5.8963 g
Wt. of bulb	5.4958
Wt. of Ca	0.4005 g
Volume of bulb	1.74 ml.
Wt. of Ca in vacuo	0.4025 g
Gram-atoms of Ca	0.1000

B. Wt. of NH_3 in calorimeter

Wt. of cylinder and NH_3	728.57 g
Wt. of cylinder	606.42
Wt. of NH_3	122.15 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	121.31 g

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings

Bottom of liquid meniscus	733.50 mm.
Reference mark	756.45 mm.
Height of reference mark from bottom of calorimeter	176.7 mm.
Height of liquid from bottom	153.7 mm.

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer reading (scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb.

(minutes)	(uv)	(scale div.)	Notes
			Manometer reading L-793.1 mm R-622.1 mm. Bath temperature 25 ±.1°C
30	1192	58.0	
31		-	Rest point 47.5
32		58.8	
33		59.2	
34	1194	49.8	
35		50.2	
36		50.5	Calorimeter line pressure
37		50.9	
38		51.2	Manometer reading L-457.6 mm R-506.5 mm.
39		51.8	
40		52.1	
41		52.6	
42		53.0	Batteries balanced
43		53.3	
44		53.6	Bulb broken
45	1188	61.0	
46		47.2	Juggling sample rod
47		54.6	Needle valve opened
48		59.4	Rest point 47.5
49		62.9	Reaction over
50		63.7	Calorimeter line pressure
51	1190	54.4	
52		54.7	Manometer reading L-455.8 mm. R-508.0 mm
53		55.3	
54		55.6	
55		55.8	
56		56.3	
57		56.7	
58.		57.0	
59		57.2	Rest point 47.6
60		56.7	
61		57.5	
62		57.8	Ammonia vaporized during solution of calcium. Gas-collecting system pressure. Manometer reading L-654.95 mm R-764.15 mm.

TABLE 5 EXPERIMENTAL DATA

EXPERIMENT B
DATE September 3, 1948
Determination of Heat
of Solution of CALCIUM
WITH LIQUID AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	6.1481 g
Wt. of bulb	5.7270
Wt. of Ca	0.4211 g
Volume of bulb	3.14 ml.
Wt. of Ca in vacuo	0.4248 g
Gram-atoms of Ca	0.106

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	718.45 g
Wt. of cylinder	606.63
Wt. of NH_3	111.82 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	110.98 g

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings

Bottom of liquid meniscus	718.80 mm
Reference mark	756.35 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	139.1 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell

Time (minutes)	Potentiometer (uv)	Galvanometer reading (scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-803.1 mm R-517.0 mm.

(minutes)	(uV)	(scale div.)	Notes
			Bath temperature 25 ±.1°C
77	1210	52.4	Rest point 62.6
78		52.7	Barometric pressure
79		52.9	764.6 mm. at 24°C
80		53.7	
81		53.4	Calorimeter line
82		53.4	pressure
83		53.6	Manometer reading
84		53.4	L-457.0 mm R-507.0 mm
85		53.6	Rest point 63.0
86		53.9	
87		54.0	
88		53.9	
89		53.7	Bulb broken
90	1208	58.5	
90½		24.5	
91	1201	44.5	Contents warming
92		35.5	
93		37.7	
94		38.0	Reaction over
95		38.8	Calorimeter line
96		39.7	pressure
97		40.6	Manometer reading
98		41.1	L-456.0 mm R-508.8 mm
99		42.1	
100		42.4	
101		42.9	
102		43.4	
103		43.5	
104		43.5	
105		44.5	
106		44.5	
107		45.7	
108		46.3	
109		46.8	
110		47.3	
111		47.8	
112		48.3	
113		48.8	
114		49.2	
115		50.4	
116		49.9	Door slammed
117		50.5	Ammonia vaporized
118		51.0	during solution of
119		51.4	calcium. Gas-collecting
			system pressure
			Manometer reading
			L-651.00 mm R-768.10 mm

TABLE 6 EXPERIMENTAL DATA

EXPERIMENT C
DATE September 23, 1948
Determination of Heat
of Solution of CALCIUM
WITH LIQUID AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	4.7212 g
Wt. of bulb	4.5073 g
Wt. of Ca	0.2139 g
Volume of bulb	3.03 ml.
Wt. of Ca in vacuo	0.2175 g
Gram-atoms of Ca	0.00544

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	728.89 g
Wt. of cylinder	615.72
Wt. of NH_3	113.17 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	112.33 g

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	722.75 mm
Reference mark	754.80 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	144.7 mm.

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-789.5 mm R-700.2 mm

(minutes)	(uv)	(scale div.)	Notes
			Bath temperature 25±.1°C
176	1206	58.3	Rest Point 43.2
177		58.9	Calorimeter line pressure
178		59.0	Manometer reading
179		59.5	L-467.0 mm R-496.3 mm
180		59.7	
181		59.6	Batteries balanced
182		59.7	
183		59.9	
184		60.1	
185		60.3	Bulb broken
185½		62.0	
186		67.0	
186¼		73.8	Warming up
186½		73.5	
187	1208	70.8	
188		63.0	Reaction over
189		64.0	
190		64.2	Calorimeter line pressure
191		64.2	Manometer reading
192		64.2	L-468.0 mm R-496.0 mm
193		64.3	
194		64.3	
195		64.3	Rest Point 43.2
			Ammonia vaporized during solution of calcium. Gas-collecting system pressure
			Manometer reading
			L-637.15 mm R-697.85 mm

TABLE 7 EXPERIMENTAL DATA

EXPERIMENT D
DATE September 28, 1948
Determination of Heat of Solution of CALCIUM WITH LIQUID AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	5.8019 g
Wt. of bulb	5.6289
Wt. of Ca	0.1731 g
Volume of bulb	2.37 ml.
Wt. of Ca in vacuo	0.1759 g
Gram-atoms of Ca	0.00440

B. Wt. of NH_3 in Calorimeter

Wt.,of cylinder and NH_3	731.48 g
Wt. of cylinder	626.74
Wt. of NH_3	104.74 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	103.90

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	715.35 mm
Reference mark	756.40 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	135.7 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-788.4 mm R-724.0 mm

(minutes)	(uv)	(scale div.)	Notes
			Bath temperature 25 ± .1°C
93	1198	54.6	
94		54.5	
95		54.5	
96		54.8	
97		55.0	
98		55.0	
99		53.4	
100		55.5	
101		55.8	
102		55.7	Rest Point 55.8
103		56.0	Calorimeter line pressure
104		56.0	Manometer reading
105		55.9	L-465.1 mm R-499.1 mm
106		56.3	Bulb broken
107		79.0	
107½		66.6	
108		66.3	
109		69.0	
110		68.5	Reaction over
111		68.2	Warming up
112		67.9	
113		67.6	Calorimeter line pressure
114		67.3	Manometer reading
115	1200	57.2	L-463.0 mm R-501.5 mm
116		56.7	
117		56.6	
118		56.6	
119		56.6	
120		56.3	Ammonia vaporized during solution of calcium. Gas-collecting system pressure Manometer reading L-648.05 mm R-702.95 mm

TABLE 8 EXPERIMENTAL DATA

EXPERIMENT E
DATE October 8, 1948
Determination of Heat of Solution of CALCIUM WITH LIQUID AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	6.1741 g
Wt. of bulb	5.9765
Wt. of Ca	0.1976 g
Volume of bulb	1.83 ml.
Wt. of Ca in vacuo	0.1998 g
Gram-atoms of Ca	0.00500

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	748.07 g
Wt. of cylinder	626.07
Wt. of NH_3	122.00 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	121.16 g

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	733.65 mm
Reference mark	757.65 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	141.3 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell

Time (minutes)	Potentiometer(uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-793.5 mm R-505.8 mm Bath temperature 25 ± .1°C

(minutes)	(uv)	(scale div.)	Notes
53	1205	56.4	Rest point 47.5
54		56.2	
55		56.3	
56		56.3	
57		56.4	
58		56.5	
59		56.7	
60		56.6	
61		56.6	
62		56.6	Calorimeter line pressure
63		56.6	Manometer reading
64		56.4	L-458.8 mm R-505.8 mm
65		56.7	Bulb broken
66	1202	7.0	
67	1190	54.5	
68		68.7	
69	1194	52.0	
70		56.3	
71		57.7	
72		58.5	Reaction over
73		59.4	Calorimeter line pressure
74		60.1	Manometer reading
75		60.6	L-454.2 mm R-510.0 mm
76		61.4	
77		62.2	
78		62.8	
79		63.4	
80		64.1	
81		64.7	Ammonia vaporized during
82		65.2	solution of calcium
			Gas-collecting system
			pressure
			Manometer reading
			L-667.65 mm R-697.85 mm

TABLE 9 EXPERIMENTAL DATA

EXPERIMENT F
DATE December,29, 1948
Determination of Heat of Solution of CALCIUM WITH LIQUID AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	4.8725 g
Wt. of bulb	4.6925
Wt. of Ca	0.1800 g
Volume of bulb	1.20 ml.
Wt. of Ca in vacuo	0.1814 g
Gram-atoms Ca	0.00452

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1026.76 g
Wt. of cylinder	914.21
Wt. of NH_3	112.55 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	111.71 g

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings

Bottom of liquid meniscus	728.85 mm
Reference mark	761.65 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	143.9 mm

E. Analysis of Calorimeter Contents

Vol. of $KMnO_4$ used in titration of 300 ml. aliquot	25.50 ml.
Wt. of Ca present (Ca metal and Ca as oxide)	0.1747 g

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature

(minutes)	(uv)	(scale div.)	Notes
			equilibrium. Gas-collecting system pressure Manometer reading L-792.6 mm R-728.0 mm Bath temperature 25 ± .1°C
90	1198	52.7	
91		52.8	
92		53.0	Rest Point 43.8
93		53.1	
94		52.9	
95		53.1	
96		53.7	
97		54.1	Rest Point 44.0
98		54.6	
99		54.5	
100		55.0	
10	1199	49.4	
102		49.9	Calorimeter line pressure
103		49.9	Manometer reading
104		50.0	L-467.2 mm R-496.8 mm
105		50.4	Rest Point 44.1
106		50.4	Bulb broken
107	1188	78.6	
108	1190	77.0	
109	1194	75.3	
110	1199	57.1	
111	1201	52.9	
112		56.5	
113		58.6	
114		61.2	
115	1203	50.5	
116		52.9	
117		52.9	Rest Point 44.6
118		52.7	
119		53.3	
120		54.8	
121		55.3	Reaction over
122		55.3	Calorimeter line pressure
123		55.5	Manometer reading
124		55.6	L-468.9 mm R-495.0 mm
125		55.7	
126		55.3	Rest Point 44.8
127		54.7	
128		54.7	
129		54.6	
130		54.6	
131		55.1	Rest Point 45.0
132		54.7	

(minutes)	(uv)	(scale div.)	Notes
133		54.7	
134		54.5	
135		54.5	
136		54.6	Ammonia vaporized during solution of calcium. Gas-collecting system pressure Mannometer reading L-654.80 mm R-709.60 mm

TABLE 10 EXPERIMENTAL DATA

EXPERIMENT G
DATE January 5, 1949
Determination of Heat of Solution of CALCIUM WITH LIQUID AMMONIA

A. Wt. of Calcium Sample

Wt. of bulb and Ca	4.4113 g
Wt. of bulb	4.2186
Wt. of Ca	0.1927 g
Volume of bulb	1.51 ml.
Wt. of Ca in vacuo	0.1945 g
Gram-atoms of Ca	0.00485

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1025.69 g
Wt. of cylinder	914.41
Wt. of NH_3	111.28 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	110.55 g

C. No Ammonium Iodide Used

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	727.05 mm
Reference mark	762.45 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	141.3 mm

E. Analysis of Calorimeter Contents

Vol. of $KMnO_4$ used in titration of 300 ml. aliquot	27.63 ml.
Wt. of Ca present (Ca metal and Ca as oxide)	0.1895 g

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer reading (scale div.)	Notes
			Ammonia vaporized as system attains temperature

(minutes)	(uv)	(scale div.)	Notes
			equilibrium. Gas-collecting system pressure. Manometer reading L-792.6mm R-728.0 mm Bath temperature 25± .1°C
30	1197	49.0	
31		49.3	Rest Point 49.2
32		49.2	Pump on
33		49.7	Calorimeter line pressure
34		49.5	Manometer reading
35		49.5	L-467.8 mm R-496.0 mm
36		49.9	Rest Point 49.7
37		50.3	
38		50.5	
39		50.5	Pump off
40		50.5	Rest Point 49.5
41		50.7	Bulb broken
42		53.0	
43	1198	47.0	
44	1199	53.0	
45	1200	50.5	
46		51.4	
47		51.0	
48		51.0	
49		51.0	Reaction over
50		50.5	
51		49.9	Calorimeter line pressure
52		49.5	Manometer reading
53		49.3	L-467.0 mm R-496.5 mm
54		49.4	
55		49.2	
56		49.0	Rest Point 50.2
57		48.5	
58		48.5	
59		48.0	
60		47.9	
61	1199	52.1	Ammonia vaporized during solution of calcium. Gas-collecting system pressure Manometer reading L-706.20 mm R-651.60 mm

TABLE 11 EXPERIMENTAL DATA

EXPERIMENT 1
DATE November 5, 1948
Determination of Heat of Reaction of CALCIUM METAL WITH AMMONIUM ION (Wire gauze used)

A. Wt. of Calcium Sample

Wt. of bulb and Ca	5.1201 g
Wt. of bulb	5.0796
Wt. of Ca	0.0405 g
Volume of bulb	1.35 ml.
Wt. of Ca in vacuo	0.0421 g
Gram-atoms of Ca	0.00105

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1031.76 g
Wt. of cylinder	914.47
Wt. of NH_3	117.29 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	116.45 g

C. Wt. of Ammonium Iodide Used

Wt. required	0.337 g
Wt. used	0.3469 g

D. Liquid Height in Calorimeter

Cathetometer readings

Bottom of liquid meniscus	726.60 mm
Reference mark	757.80 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	145.5 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-786.7 mm R-762.0 mm

(minutes)	(uv)	(scale div.)	Notes
			Bath temperature 25 ± .1°C
30	1202	55.2	
31		55.5	
32		55.8	
33		56.1	Batteries balanced
34		56.3	Rest Point 46.0
35		56.7	
36		56.9	
37		57.2	
38		57.4	Rest Point 46.3
39		57.5	
40		57.9	
41		58.0	Calorimeter line pressure
42		58.2	Manometer reading
43		58.4	L-469.0 mm R-494.8 mm
44		58.5	
45		58.8	
46		58.9	Bulb broken
47	1199	60.0	
48	1201	60.2	Reaction very slow
49	1205	60.0	
50	1206	59.3	
51	1209	83.1	
52	1219	56.3	
53	1219	58.0	
54	1220	54.1	
55		55.2	
56		55.7	Still reacting - blue color
57		57.0	under platinum gauze
58		56.9	
59		57.8	
60	1222	47.6	Reaction apparently over
61		47.0	but still blue under gauze
62		46.5	
63		45.7	
64		44.9	
65		44.2	
66		43.5	
67	1220	53.5	Calorimeter line pressure
68		52.9	Manometer reading
69		52.5	L-468.9 mm R-495.0 mm
70		51.8	
71		51.4	
72		51.0	Ammonia vaporized during
73		50.2	reaction of calcium. Gas-
74		49.6	collecting system pressure
75		48.8	Manometer reading
			L-635.5 mm R-720.0 mm.

(minutes)	(uv)	(scale div.)	Notes
			At the end of the experiment there was still a blue solution trapped under the wire gauze.

TABLE 12 EXPERIMENTAL DATA

EXPERIMENT 2
DATE November 9, 1948
Determination of Heat of Reaction of CALCIUM METAL WITH AMMONIUM ION (Wire gauze used)

A. Wt. of Calcium Sample

Wt. of bulb and Ca	5.8749 g
Wt. of bulb	5.8372
Wt. of Ca	0.0377 g
Volume of bulb	1.97 ml.
Wt. of Ca in vacuo	0.0400 g
Gram-atoms of Ca	0.00100

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1030.95 g
Wt. of cylinder	914.43
Wt. of NH_3	116.52 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	115.68 g

C. Wt. of Ammonium Iodide Used

Wt. required	0.319 g
Wt. used	0.3200 g

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	726.90 mm
Reference mark	757.80 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	145.8 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentio-meter (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-760.0 mm R-732.8 mm Bath temperature 25 ± .1°C

(minutes)	(uv)	(scale div.)	Notes
50	1204	54.0	Rest point 52.4
51		54.5	
52		54.0	
53		54.0	
54		54.4	
55		54.0	
56		53.5	
57		53.7	
58		54.1	
59		53.7	
60		53.6	
61		53.8	
62		54.0	
63		54.9	
64		54.8	
65		54.5	Calorimeter line pressure
66		54.7	Manometer reading
67		54.6	L-455.6 mm R-509.00 mm
68		54.5	
69		- -	Telescope bumped
70		55.3	Rest Point 52.5
71		55.5	
72		56.0	
73		56.0	Bulb broken
74	1200	51.0	
75		49.5	Rest Point 52.8
76		54.0	Reaction very slow
77	1201	49.5	Blue solution under gauze
78		55.6	
79	1202	54.4	
80		56.1	
81	1203	53.0	
82		53.7	Batteries balanced
83		53.9	
84		55.0	
85	1201	55.0	Shaking sample rod
86	1203	55.0	
87	1204	56.1	
88	1205	54.7	Rest Point 53.0
89		56.6	
90		57.4	Reaction over
91		57.2	
92		52.0	
93		52.3	Calorimeter line pressure
94		52.3	Manometer reading
95		51.8	L-455.2 mm R-509.4 mm
96		52.0	
97		52.3	

(minutes)	(uv)	(scale div.)	Notes
98		52.2	
99		52.4	
100		52.7	
101		53.0	
102		52.7	
103		52.6	
104		52.9	
105		52.9	
106		53.1	
107		52.8	
108		53.0	
109		52.8	
110		53.5	
111		53.0	
112		52.7	
113		52.4	
114		52.6	
115		53.0	
116		53.1	
117		53.2	Ammonia vaporized during reaction of calcium. Gas-collecting system pressure. Manometer reading L-645.25 mm R-694.20 mm At the end of the experiment there was still a blue solution trapped under the wire gauze.

TABLE 13 EXPERIMENTAL DATA

EXPERIMENT 3
DATE November 18, 1948
Determination of Heat
of Reaction of CALCIUM METAL
WITH AMMONIUM ION
(No wire gauze used)

A. Wt. of Calcium Sample

Wt. of bulb and Ca	3.3478 g
Wt. of bulb	3.3113
Wt. of Ca	0.0365 g
Volume of bulb	12.24 ml.
Wt. of Ca in vacuo	0.0380 g
Gram-atoms Ca	0.00095

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1031.70 g
Wt. of cylinder	914.13
Wt. of NH_3	117.57 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH3 in calorimeter	116.73 g

C. Wt. of Ammonium Iodide Used

Wt. required	0.304 g
Wt. used	0.3621 g

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	729.55 mm
Reference mark	759.60 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	146.7 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer readings (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-780.0 mm R-723.0 mm

(minutes)	(uv)	(scale div.)	Notes
			Bath temperature 25 ±.1°C
41	1200	53.5	Rest Point 53.6
42		53.7	
43		53.9	
44		54.1	
45		54.1	Calorimeter line pressure
46		54.2	Manometer reading
47		54.6	L-469.3 mm R-494.8 mm
48		54.4	
49		54.8	
50		55.0	Bulb broken
51	1198	58.5	Rapid reaction but no
52	1219	59.0	foaming
53	1221	53.3	
54		53.6	
55		53.1	
56		51.5	
57		50.7	
58		49.9	Reaction over
59		49.3	Calorimeter line pressure
60		48.6	Manometer reading
61		47.8	L-469.8 mm R-494.5 mm
62	1220	52.3	
63		51.5	
64		50.7	
65		50.2	Ammonia vaporized during reaction of calcium. Gas-collecting system pressure. Manometer reading L-643.25 mm R-732.90 mm

TABLE 14 EXPERIMENTAL DATA

EXPERIMENT 4
DATE November 26, 1948
Determination of Heat of Reaction of CALCIUM METAL WITH AMMONIUM ION (No wire gauze used)

A. Wt. of Calcium Sample

Wt. of bulb and Ca	4.4296 g
Wt. of bulb	4.3938
Wt. of Ca	0.0358 g
Volume of bulb	1.51 ml.
Wt. of Ca in vacuo	0.0376 g
Gram-atoms of Ca	0.000938

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1031.92 g
Wt. of cylinder	914.44
Wt. of NH_3	117.48 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	116.64 g

C. Wt. of Ammonium Iodide Used

Wt. required	o.300 g
Wt. used	0.3581 g

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	730.50 mm
Reference mark	761.70 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	145.5 mm

E. Analysis of Calorimeter Contents

Vol. of $KMnO_4$ used in titration of 300 ml. aliquot	5.02 ml.
Wt. of Ca present (Ca metal and Ca as oxide)	0.0343 g

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as

(minutes)	(uv)	(scale div.)	Notes
			system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-784.0 mm R-750.3 mm Bath temperature 25±.1°C
32	1199	50.8	
33		51.1	Rest Point 49.9
34		51.3	
35		51.5	Calorimeter line pressure
36	1200	46.9	Manometer reading
37		46.9	L-467.9 mm R-496.0 mm
38		47.0	
39		47.0	
40		47.4	Rest Point 50.4
41		47.3	
42		47.6	
43		47.7	Bulb broken
44	1217	48.7	
45	1220	46.0	Blue streaks near bulb
46		47.7	
47		48.4	
48		48.5	
49		47.6	
50	1219	52.0	Rest Point 50.0
51		51.2	Reaction over
52		50.2	
53		49.6	Calorimeter line pressure
54		48.9	Manometer reading
55		48.0	L-468.0 mm R-495.7 mm
56		47.2	
57		46.7	
58		46.0	
59		45.3	
60		44.8	
61		44.1	Ammonia vaporized during
62		43.5	reaction of calcium. Gas-
63		42.4	collecting system pressure
			Manometer reading
			L-652.65 mm R-738.45 mm

TABLE 15 EXPERIMENTAL DATA

EXPERIMENT 5
DATE December 15, 1948
Determination of Heat of Reaction of CALCIUM METAL WITH AMMONIUM ION (No wire gauze used)

A. Wt. of Calcium Sample

Wt. of bulb and Ca	4.4344 g
Wt. of bulb	4.3969 g
Wt. of Ca	0.0375 g
Volume of bulb	1.77 ml.
Wt. of Ca in vacuo	0.0396 g
Gram-atoms of Ca	0.000988

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1031.87 g
Wt. of cylinder	914.21
Wt. of NH_3	117.66 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	116.82 g

C. Wt. of Ammonium Iodide Used

Wt. required	0.317 g
Wt. used	0.3200 g

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	727.80 mm
Reference mark	759.70 mm
Height of reference mark from bottom of calorimeter	176.7 mm
Height of liquid from bottom	144.8 mm

E. Analysis of Calorimeter Contents

Vol. of $KMnO_4$ used in titration of 300 ml. aliquot	18.84 ml.
Wt. of Ca present (Ca metal and Ca as oxide)	0.0388 g

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as

(minutes)	(uv)	(scale div.)	Notes
			system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-774.3 mm R-717.1 mm Bath temperature 25 ±.1°C
10	1196	51.6	
11		51.9	Rest Point 49.2
12		51.9	Barometric pressure 772.3 mm
13		52.0	
14		51.5	
15		51.9	
16		52.2	
17		52.1	
18		52.1	
19		52.4	
20		52.5	Rest Point 48.8
21		52.5	
22		53.0	Batteries balanced
23		52.3	
24		53.0	
25		52.4	
26		52.5	
27		53.5	
28		52.8	
29		53.0	
30		53.1	
31		52.6	
32		53.1	
33		53.5	Calorimeter line pressure
34		54.0	Manometer reading
35		53.7	L-467.9 mm R-496.9 mm
36		53.9	
37		54.5	
38		53.8	Batteries balanced
39		5318	
40		54.7	Bulb broken
41	1206	51.5	
42	1209	68.4	
43	1215	54.5	
44		56.5	
45	1216	53.2	
46		53.4	Reaction almost over but
47		53.0	blue solution on bottom
48		52.3	of bulb

(minutes)	(uv)	(scale div.)	Notes
49		50.8	Shaking sample rod
50		50.0	
51		49.0	
52		48.2	
53		45.7	
54		45.2	
55		44.3	
56		43.0	Shaking sample rod
57		42.5	
58		41.5	
59		41.3	
60		40.8	
61		38.0	
62	1214	50.6	
63		49.5	
64		48.9	
65		47.7	
66		47.8	
67		47.5	
68		46.0	
69		46.2	
70		44.0	No blue solution left
71		43.8	Calorimeter line pressure
72		46.0	Manometer reading
73		49.0	L-468.0 mm R-496.0 mm
74		52.5	Window opened
75		50.4	Window closed
76		46.6	Batteries balanced
77		43.5	
78	1213	48.3	Rest Point 50.0
79		47.3	
80		45.9	
81		45.4	Rest Point 49.4
82		44.4	
83		43.6	
84		42.7	
85		42.2	
86		42.4	
87		41.3	
88		40.9	Ammonia vaporized during reaction of calcium. Gas-collecting system pressure Manometer reading L-651.25 mm R-740.35 mm
89		40.1	
90		39.6	

TABLE 16 EXPERIMENTAL DATA

EXPERIMENT:
DATE October 23, 1948
Determination of Heat of Solution of AMMONIUM BROMIDE WITH LIQUID AMMONIA

A. Wt. of Ammonium Bromide

Wt. of bulb and NH_4Br	10.1453 g
Wt. of bulb	5.8562
Wt. of NH_4Br	4.2891 g
Volume of bulb	3.72 ml.
Wt. of NH_4Br in vacuo	4.2935 g
Gram-atoms of NH_4Br	0.0438

B. Wt. of NH_3 in Calorimeter

Wt. of cylinder and NH_3	1028.84 g
Wt. of cylinder	914.60
Wt. of NH_3	114.24 g
Volume of line	800 ml.
NH_3 in line	0.84 g
Wt. of NH_3 in calorimeter	113.40 g

C.

D. Liquid Height in Calorimeter

Cathetometer readings	
Bottom of liquid meniscus	723.40 mm
Reference mark	758.65 mm
Height of reference mark from bottom of calorimeter	176.7mm
Height of liquid from bottom	141.5 mm

E. No analysis of calorimeter contents

F. E.M.F. Measurements

Potentiometer battery circuit balanced with respect to standard cell.

Time (minutes)	Potentiometer (uv)	Galvanometer reading (Scale div.)	Notes
			Ammonia vaporized as system attains temperature equilibrium. Gas-collecting system pressure before breaking of the bulb. Manometer reading L-783.6 mm R-712.3 mm

(minutes)	(uv)	(scale div.)	Notes
			Bath temperature 25 ±.1°C
30	1198	52.9	
31		53.0	Rest Point 42.1
32		53.0	
33		53.1	
34	1199	47.6	
35		47.8	
36		47.9	
37		48.2	
38		48.4	
39		48.8	Calorimeter line pressure
40		48.8	Manometer reading
41		48.9	L-471.0 mm R-492.5 mm
42		49.3	
43		49.2	
44		49.2	Rest Point 41.5
45		49.2	
46		49.6	
47	1169	16.5	Bulb broken
48		40.8	
49		52.5	Some sample stuck in bulb
50		30.0	Sample rod shaken
51		80.0	All sample off bulb
52	1178	60.9	Gas withdrawn
53		76.7	
54		90.0	
55¼		96.7	
56		99.0	
57		99→	
58	1188	53.3	
59		53.8	Reaction over
60		54.2	Calorimeter line pressure
61		54.8	Manometer reading
62		55.0	L-469.1 mm R-494.5 mm
63		55.8	
64		56.6	
65		57.0	
66		57.7	
67		58.3	
68		59.0	Ammonia vaporized during
69		59.2	solution of ammonium
70		60.1	bromide. Gas-collecting system
71		60.9	pressure
72		61.3	Manometer reading
73		62.0	L-630.90 mm R-808.60 mm

IV. CALCULATIONS

The heat of reaction or solution is represented as the sum of the heat effects accompanying (1) the temperature change of the calorimeter and its contents, and (2) the vaporization of the ammonia collected in the gas-collecting system during the reaction period.

The heat effect associated with the temperature change of the calorimeter and its contents is calculated by multiplication of the total heat capacity of the system and the observed temperature change of the calorimeter.

A. Calculation of the Temperature Change

In this research the method described by White[21] is used to calculate the temperature change of the calorimeter and its contents. This method takes into consideration the heat added to or removed from the calorimeter and the heat added or lost due to leakage through the walls of the calorimeter. The observed temperature change is the sum of these two factors.

To get the temperature pattern the thermocouple EMF's recorded during the course of the experiment are plotted as a function of time and a smooth curve drawn through the points. The observed temperature change, ΔⒽ , is obtained as the

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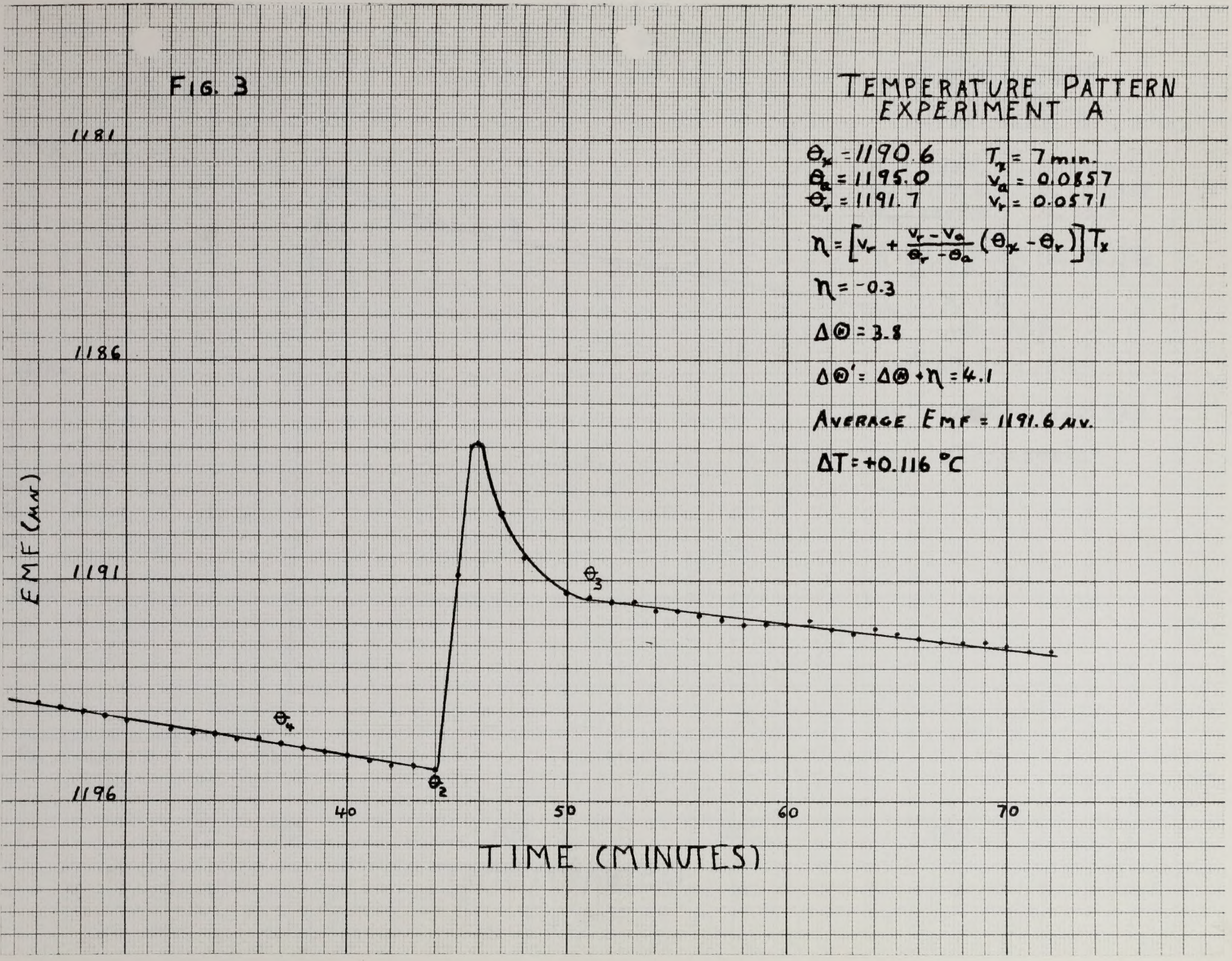
[21] White, M.P., The Modern Calorimeter, ACS Monograph Series, Chemical Catalogue Co., N.Y., 1928

FIG. 3



TEMPERATURE PATTERN
EXPERIMENT A

$\Theta_x = 1190.6$ $T_x = 7$ min.

$\Theta_a = 1195.0$ $v_a = 0.0857$

$\Theta_r = 1191.7$ $v_r = 0.0571$

$$\eta = \left[v_r + \frac{v_r - v_a}{\Theta_r - \Theta_a} (\Theta_x - \Theta_r) \right] T_x$$

$\eta = -0.3$

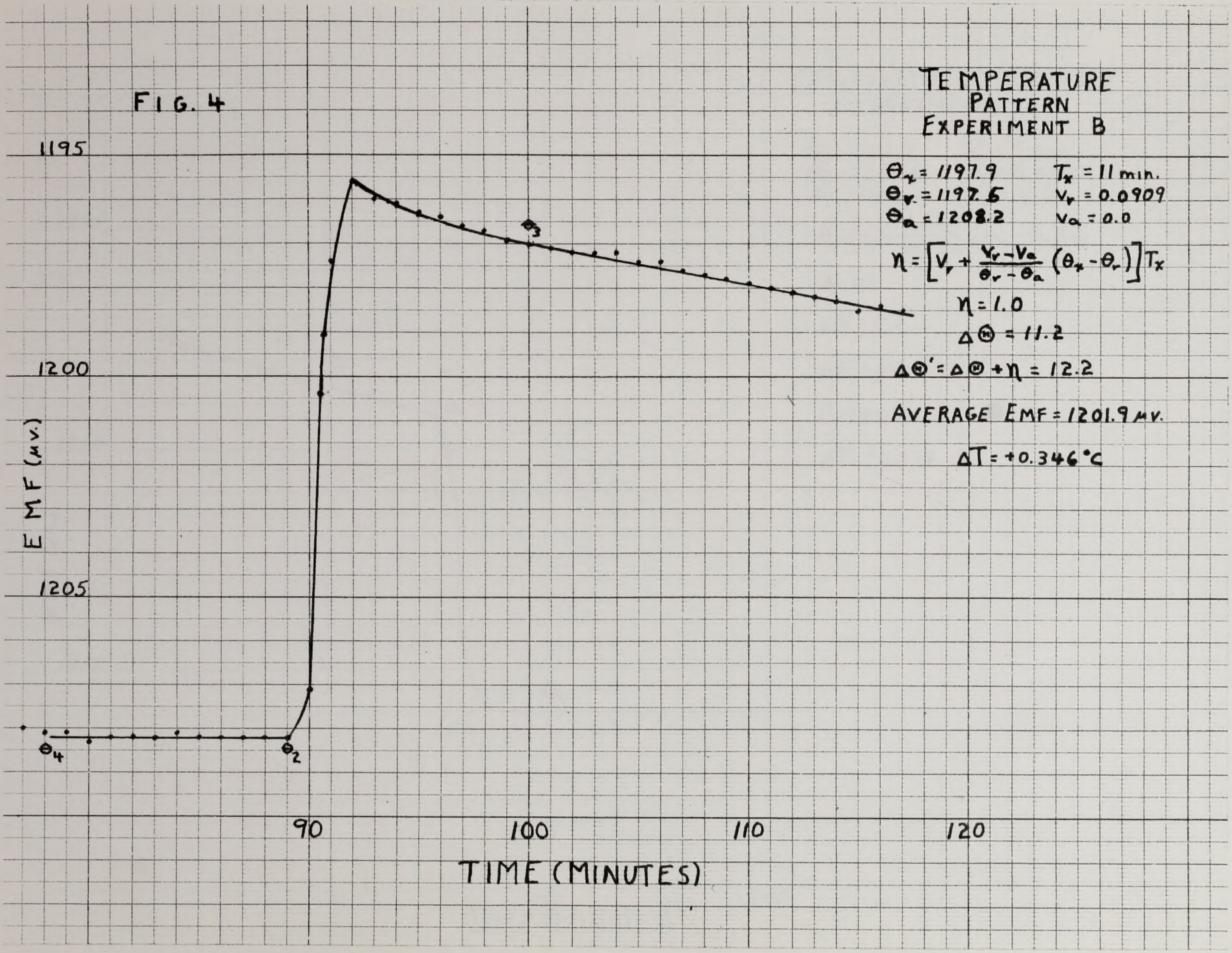
$\Delta\Theta = 3.8$

$\Delta\Theta' = \Delta\Theta + \eta = 4.1$

AVERAGE EMF = 1191.6 μv.

$\Delta T = +0.116$ °C

FIG. 4



TEMPERATURE
PATTERN
EXPERIMENT B

$\theta_x = 1197.9$ $T_x = 11$ min.
$\theta_r = 1197.6$ $V_r = 0.0909$
$\theta_a = 1208.2$ $V_a = 0.0$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right]T_x$$

$\eta = 1.0$

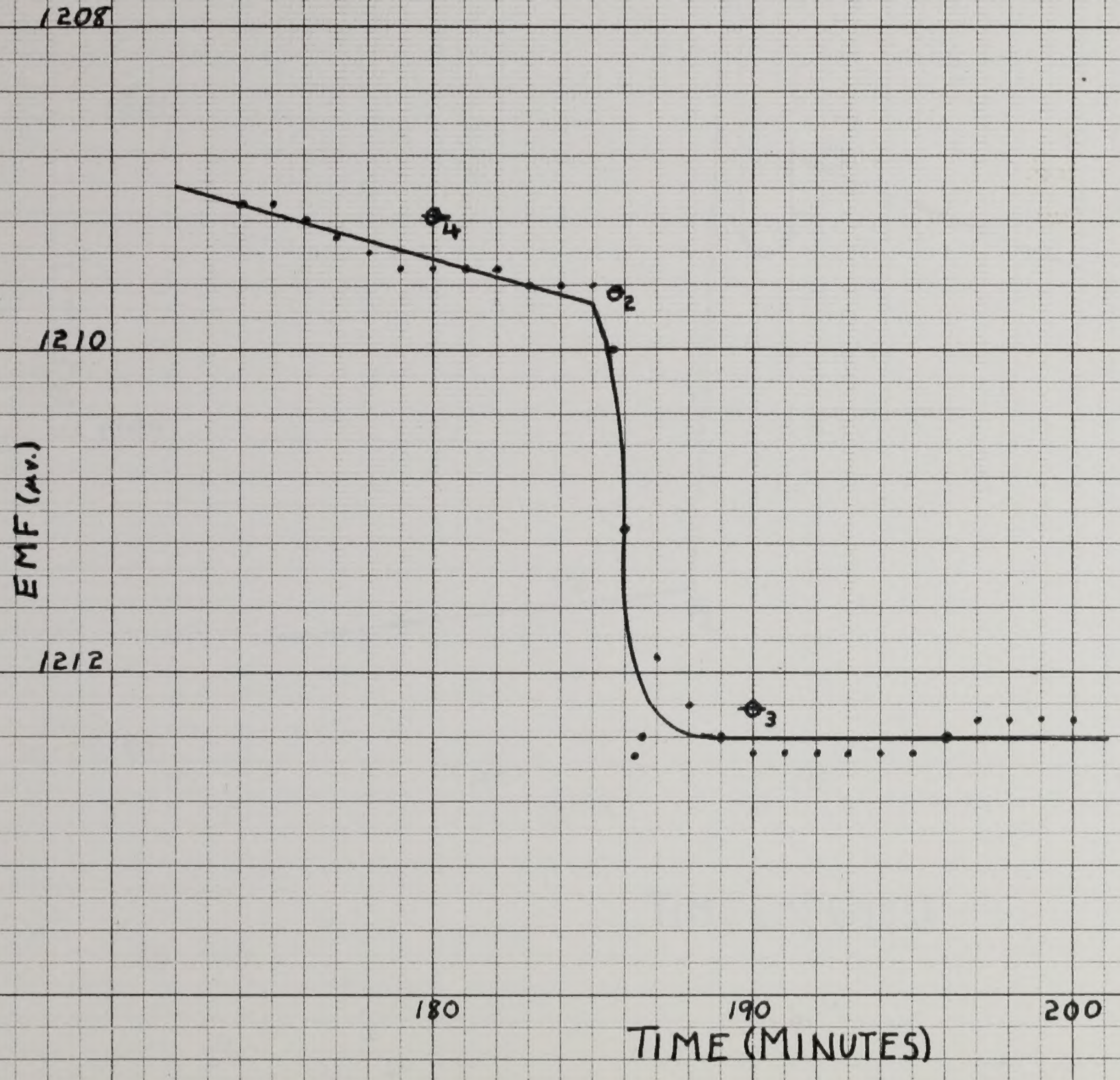
$\Delta\Theta = 11.2$

$\Delta\Theta' = \Delta\Theta + \eta = 12.2$

AVERAGE EMF = 1201.9 μv.

$\Delta T = +0.346\,^\circ C$

FIG. 5



TEMPERATURE PATTERN
EXPERIMENT C

$\Theta_x = 1211.7$ $\quad T_x = 5$ min.
$\Theta_a = 1209.6$ $\quad V_a = 0.0600$
$\Theta_r = 1212.4$ $\quad V_r = 0.0$

$$\eta = \left[V_r + \frac{V_r - V_a}{\Theta_r - \Theta_a} (\Theta_x - \Theta_r) \right] T_x$$

$\eta = 0.1$

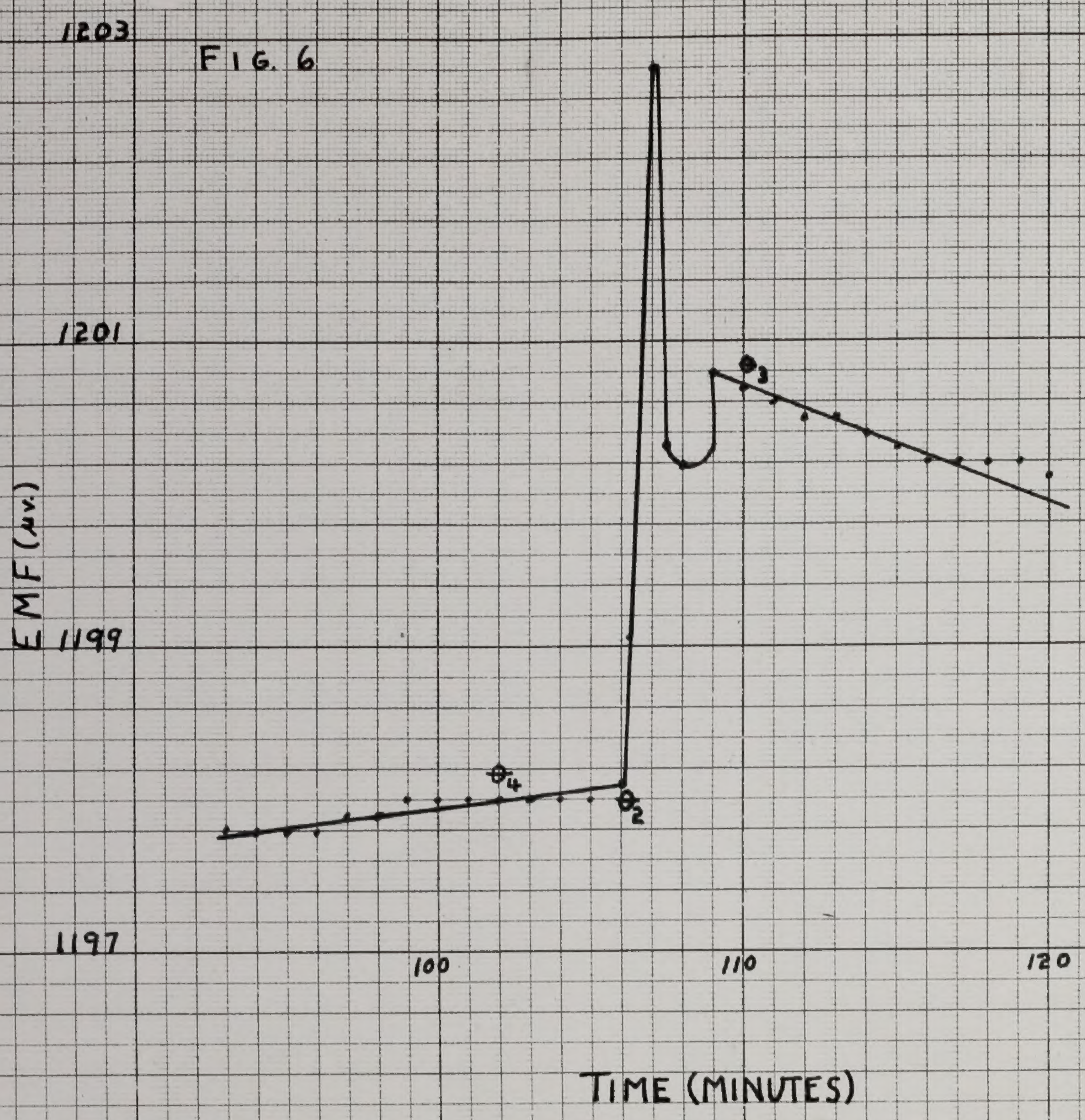
$\Delta\Theta = 2.7$

$\Delta\Theta' = \Delta\Theta + \eta = 2.8$

AVERAGE EMF = 1211.1 mv.

$\Delta T = -0.078$ °C

FIG. 6



TEMPERATURE PATTERN
EXPERIMENT D

$\theta_x = 1200.8$ $T_x = 4$ min.
$\theta_a = 1198.0$ $V_a = 0.025$
$\theta_r = 1200.6$ $V_r = -0.075$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right] T_x$$

$\eta = 0.3$

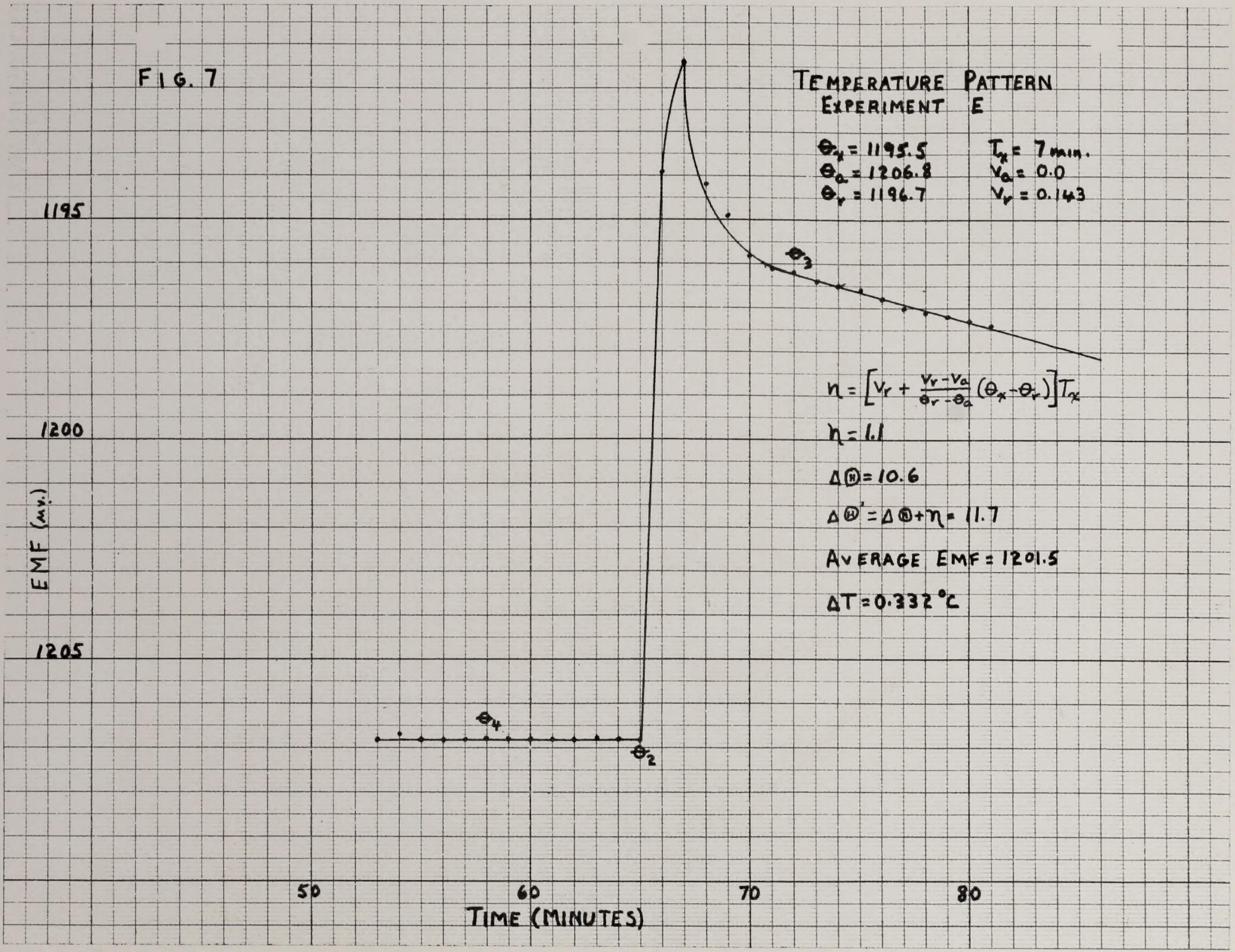
$\Delta\Theta = 2.6$

$\Delta\Theta' = \Delta\Theta + \eta = 2.9$

AVERAGE EMF = 1199.4 μv.

$\Delta T = -0.082$ °C

FIG. 7



TEMPERATURE PATTERN
EXPERIMENT E

$\Theta_x = 1195.5$ $T_x = 7$ min.
$\Theta_a = 1206.8$ $V_a = 0.0$
$\Theta_r = 1196.7$ $V_r = 0.143$

$$\eta = \left[V_r + \frac{V_r - V_a}{\Theta_r - \Theta_a}(\Theta_x - \Theta_r)\right]T_x$$

$\eta = 1.1$

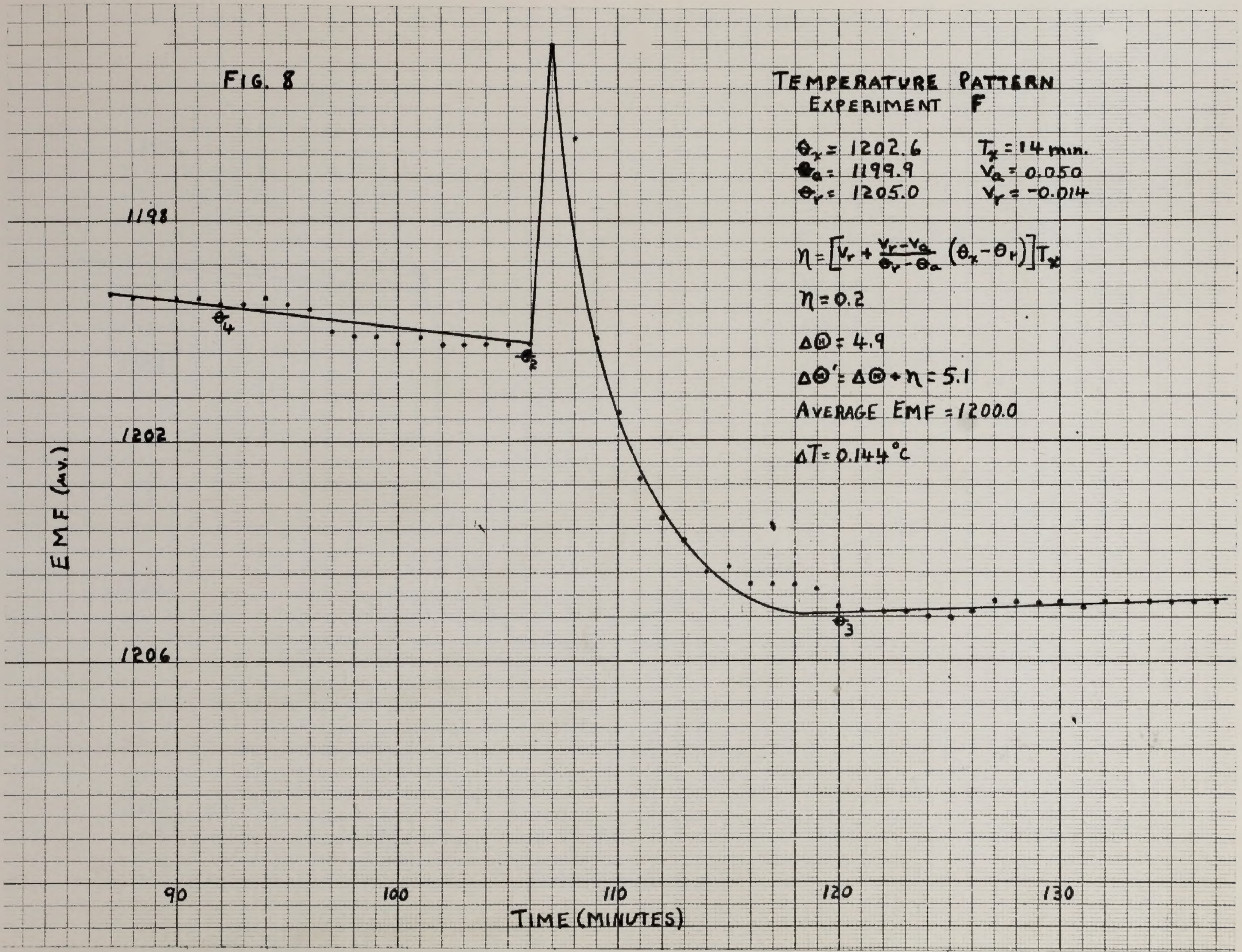
$\Delta\Theta = 10.6$

$\Delta\Theta' = \Delta\Theta + \eta = 11.7$

AVERAGE EMF = 1201.5

$\Delta T = 0.332$ °C

FIG. 8



TEMPERATURE PATTERN
EXPERIMENT F

$\theta_x = 1202.6$ $T_x = 14$ min.
$\theta_a = 1199.9$ $V_a = 0.050$
$\theta_r = 1205.0$ $V_r = -0.014$

$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right]T_x$

$\eta = 0.2$

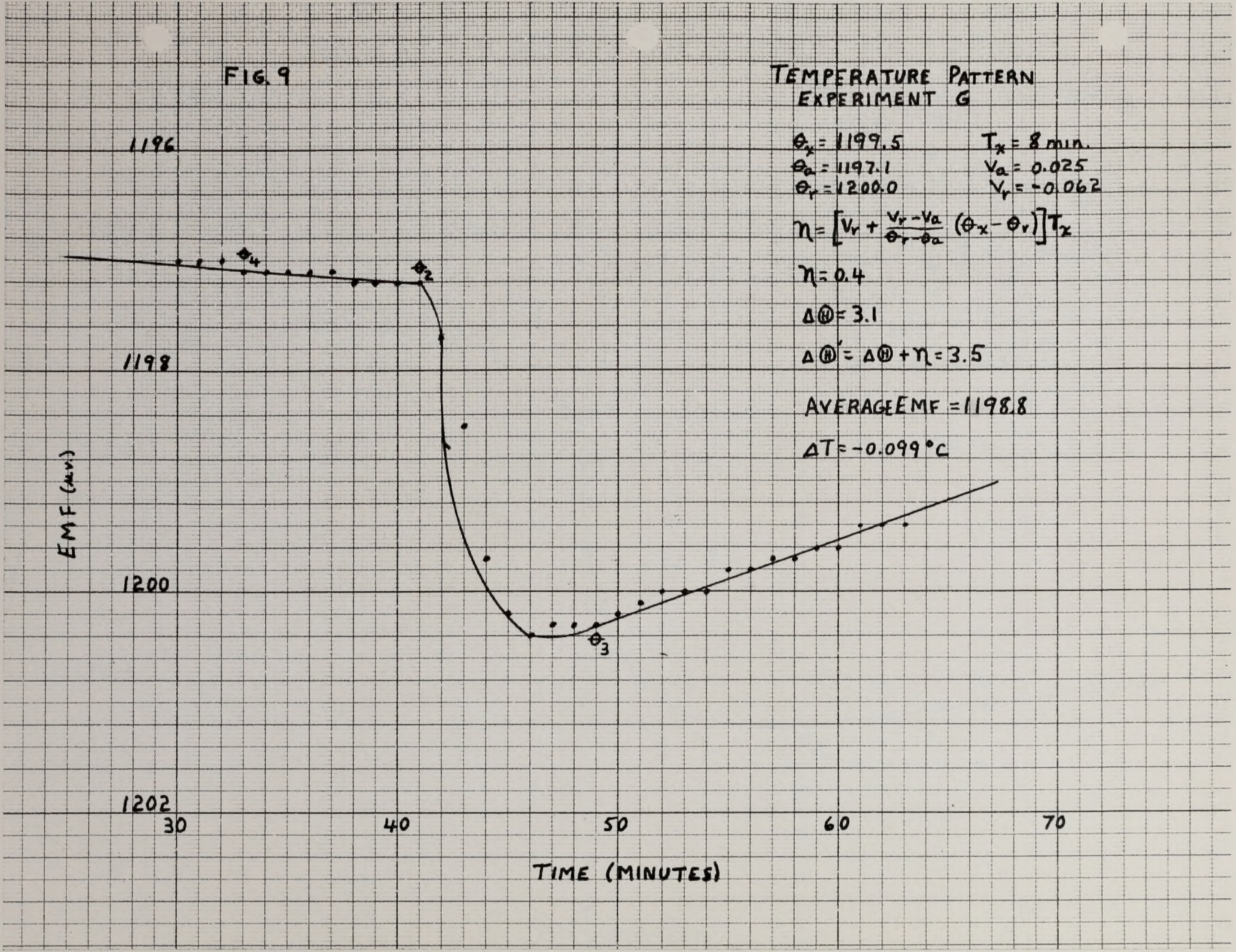
$\Delta\Theta = 4.9$

$\Delta\Theta' = \Delta\Theta + \eta = 5.1$

AVERAGE EMF = 1200.0

$\Delta T = 0.144\,^\circ C$

FIG. 9



TEMPERATURE PATTERN
EXPERIMENT G

$\Theta_x = 1199.5$ $T_x = 8$ min.

$\Theta_a = 1197.1$ $V_a = 0.025$

$\Theta_r = 1200.0$ $V_r = -0.062$

$$\eta = \left[V_r + \frac{V_r - V_a}{\Theta_r - \Theta_a}(\Theta_x - \Theta_r)\right]T_x$$

$\eta = 0.4$

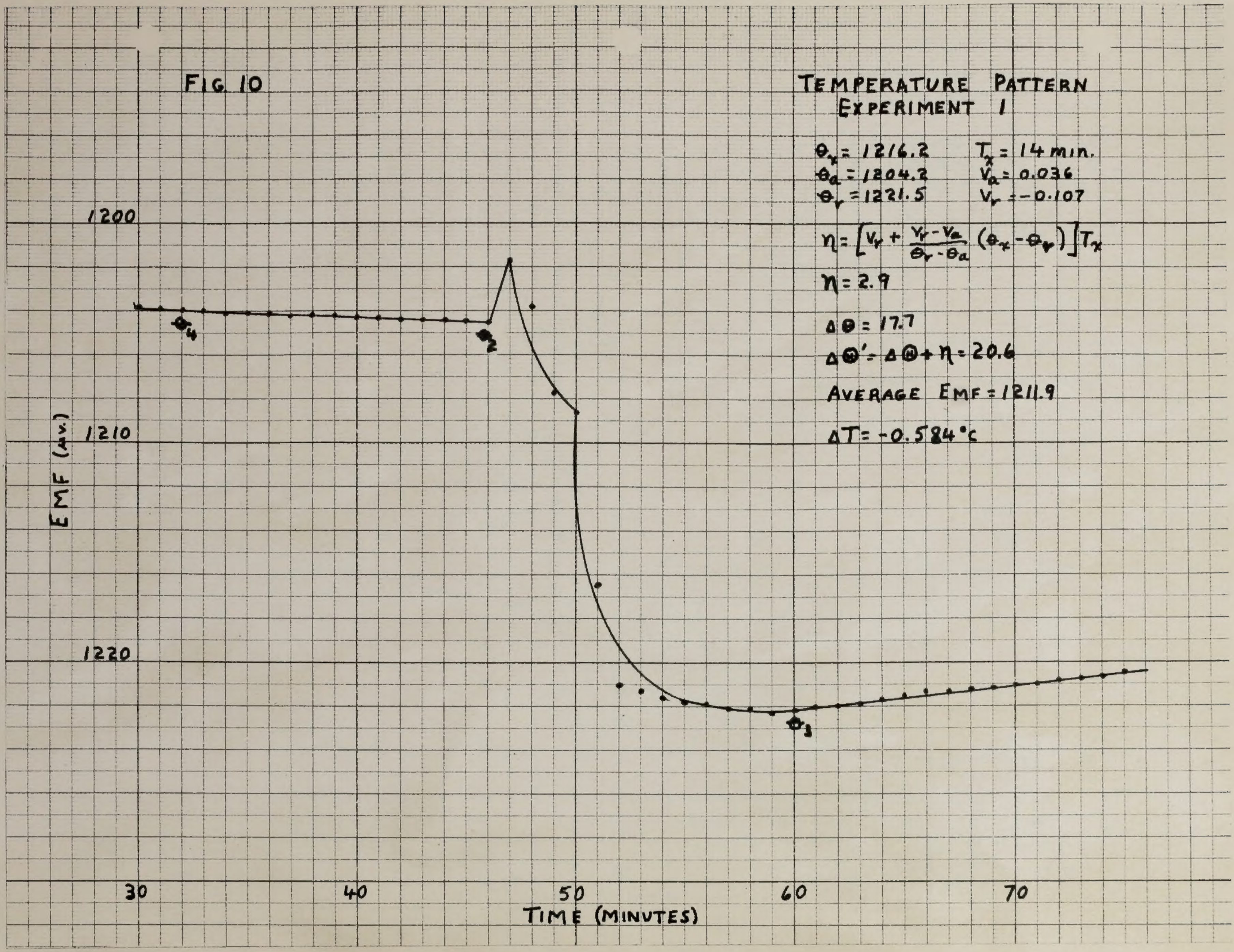
$\Delta \Theta = 3.1$

$\Delta \Theta' = \Delta \Theta + \eta = 3.5$

AVERAGE EMF = 1198.8

$\Delta T = -0.099$ °C

FIG 10



TEMPERATURE PATTERN
EXPERIMENT 1

$\theta_x = 1216.2$ $T_x = 14$ min.
$\theta_a = 1204.2$ $V_a = 0.036$
$\theta_r = 1221.5$ $V_r = -0.107$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right]T_x$$

$\eta = 2.9$

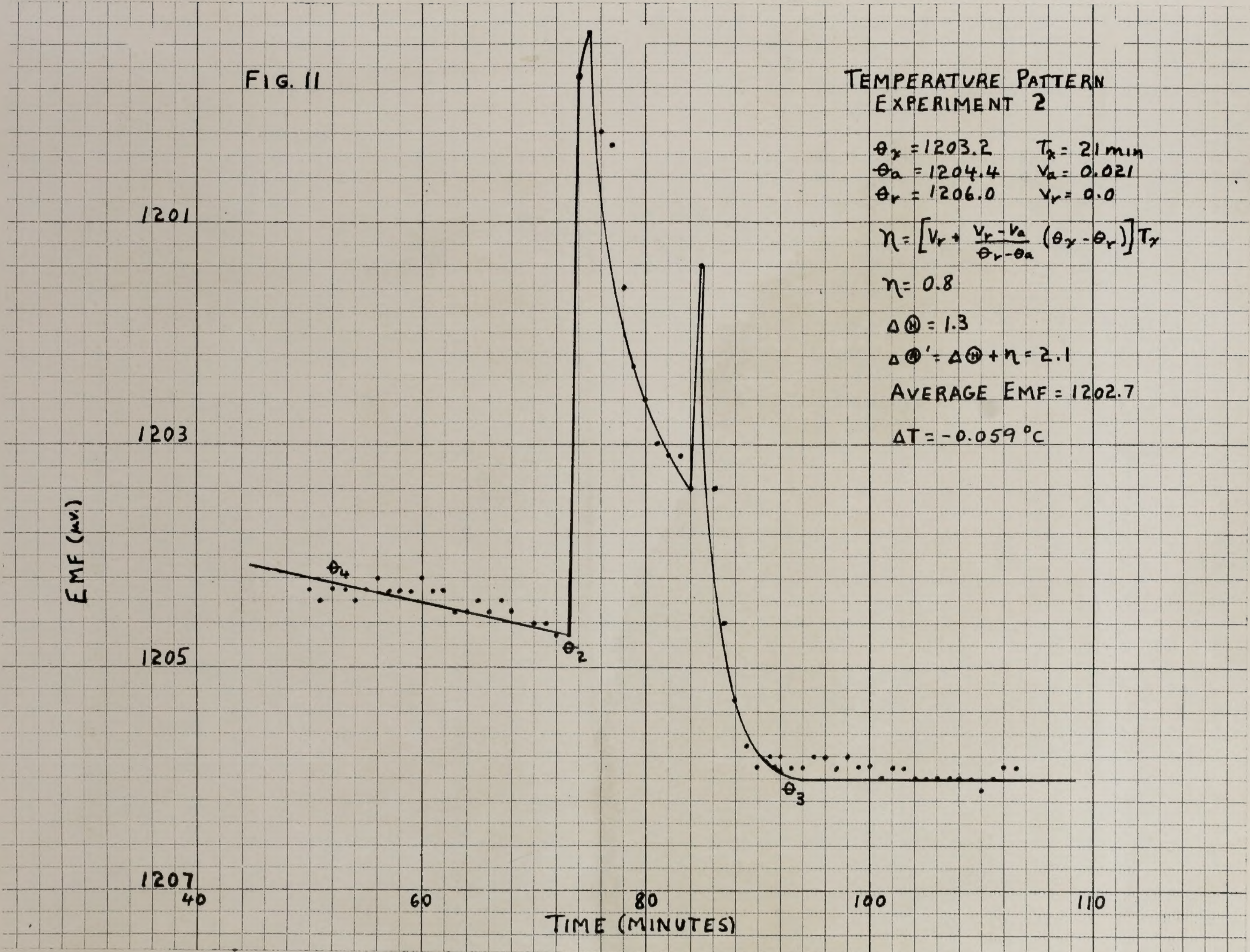
$\Delta\theta = 17.7$

$\Delta\Theta' = \Delta\Theta + \eta = 20.6$

AVERAGE EMF = 1211.9

$\Delta T = -0.584$ °C

FIG. 11



TEMPERATURE PATTERN
EXPERIMENT 2

$\theta_x = 1203.2$ $T_x = 21$ min
$\theta_a = 1204.4$ $V_a = 0.021$
$\theta_r = 1206.0$ $V_r = 0.0$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right] T_x$$

$\eta = 0.8$

$\Delta\Theta = 1.3$

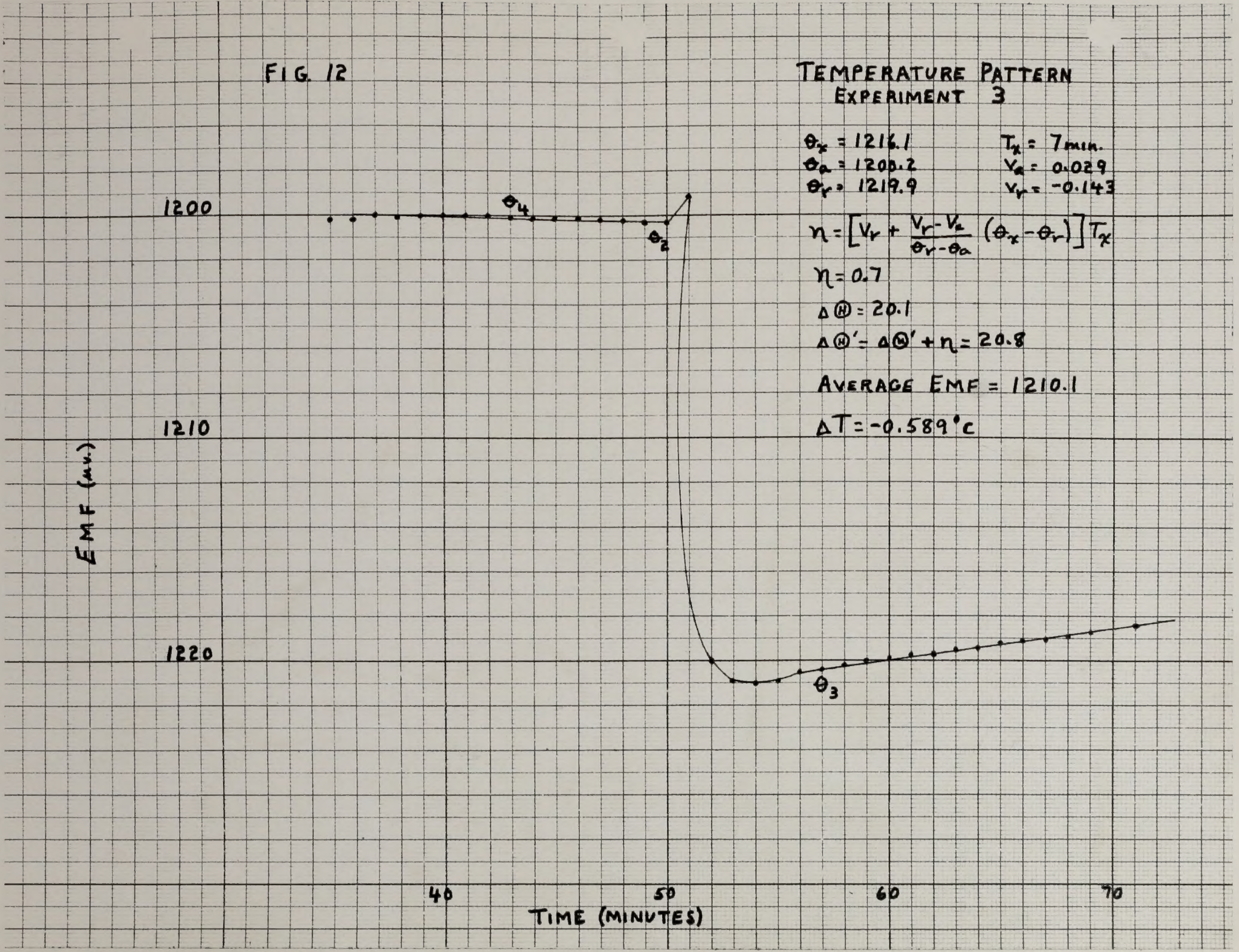
$\Delta\Theta' = \Delta\Theta + \eta = 2.1$

AVERAGE EMF = 1202.7

$\Delta T = -0.059$ °C

FIG. 12

TEMPERATURE PATTERN
EXPERIMENT 3



$\theta_x = 1216.1$
$\theta_a = 1200.2$
$\theta_r = 1219.9$

$T_x = 7$ min.
$V_a = 0.029$
$V_r = -0.143$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right] T_x$$

$\eta = 0.7$

$\Delta \Theta = 20.1$

$\Delta \Theta' = \Delta \Theta' + \eta = 20.8$

AVERAGE EMF = 1210.1

$\Delta T = -0.589°C$

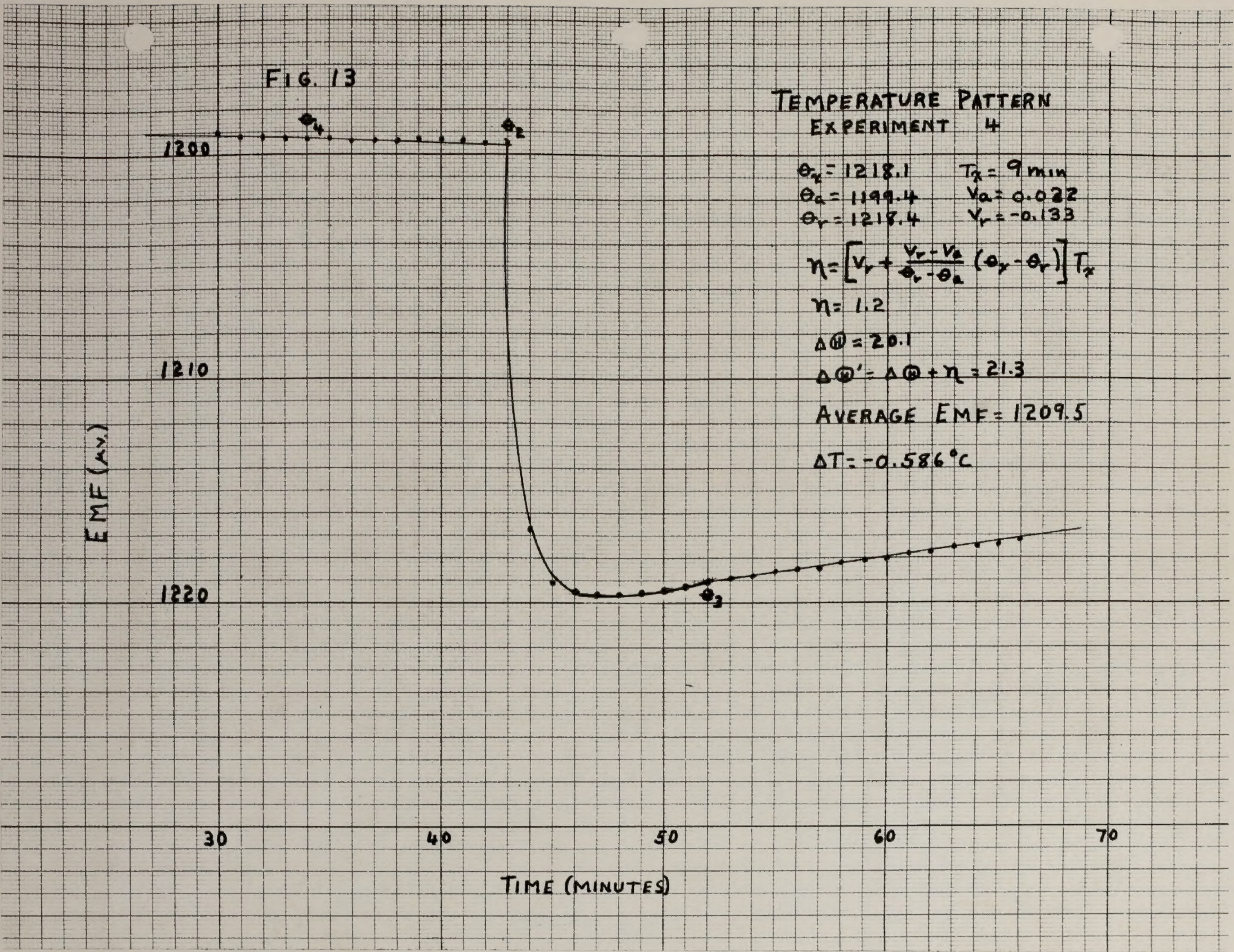


FIG. 13

TEMPERATURE PATTERN
EXPERIMENT 4

$\theta_x = 1218.1$ $T_x = 9$ min
$\theta_a = 1199.4$ $V_a = 0.022$
$\theta_r = 1218.4$ $V_r = -0.133$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right] T_x$$

$\eta = 1.2$

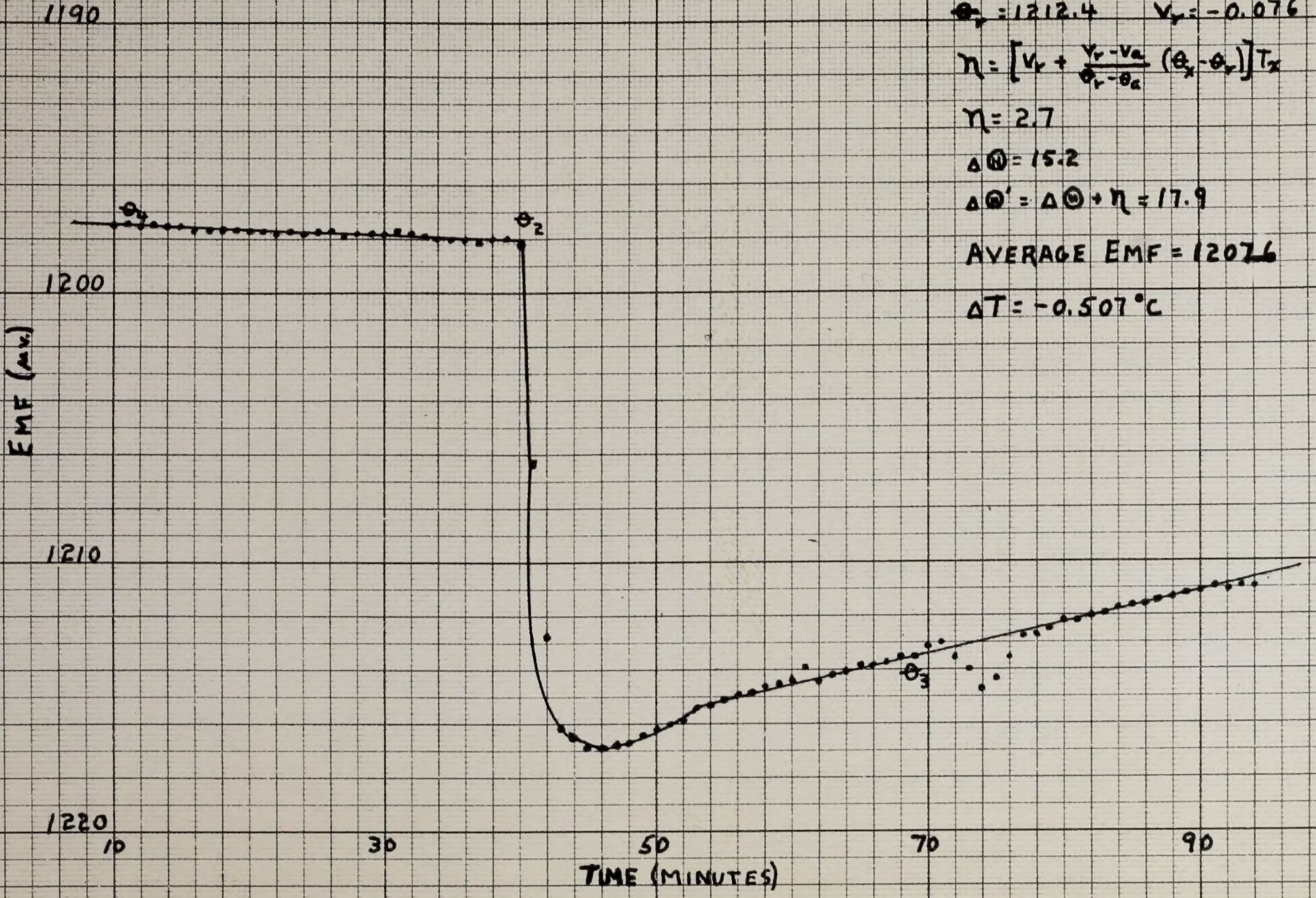
$\Delta\Theta = 20.1$

$\Delta\Theta' = \Delta\Theta + \eta = 21.3$

AVERAGE EMF = 1209.5

$\Delta T = -0.586$ °C

FIG. 14



TEMPERATURE PATTERN
EXPERIMENT 5

$\theta_x = 1214.6$ $T_x = 29$ min.
$\theta_a = 1197.8$ $V_a = 0.028$
$\theta_r = 1212.4$ $V_r = -0.076$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right]T_x$$

$\eta = 2.7$

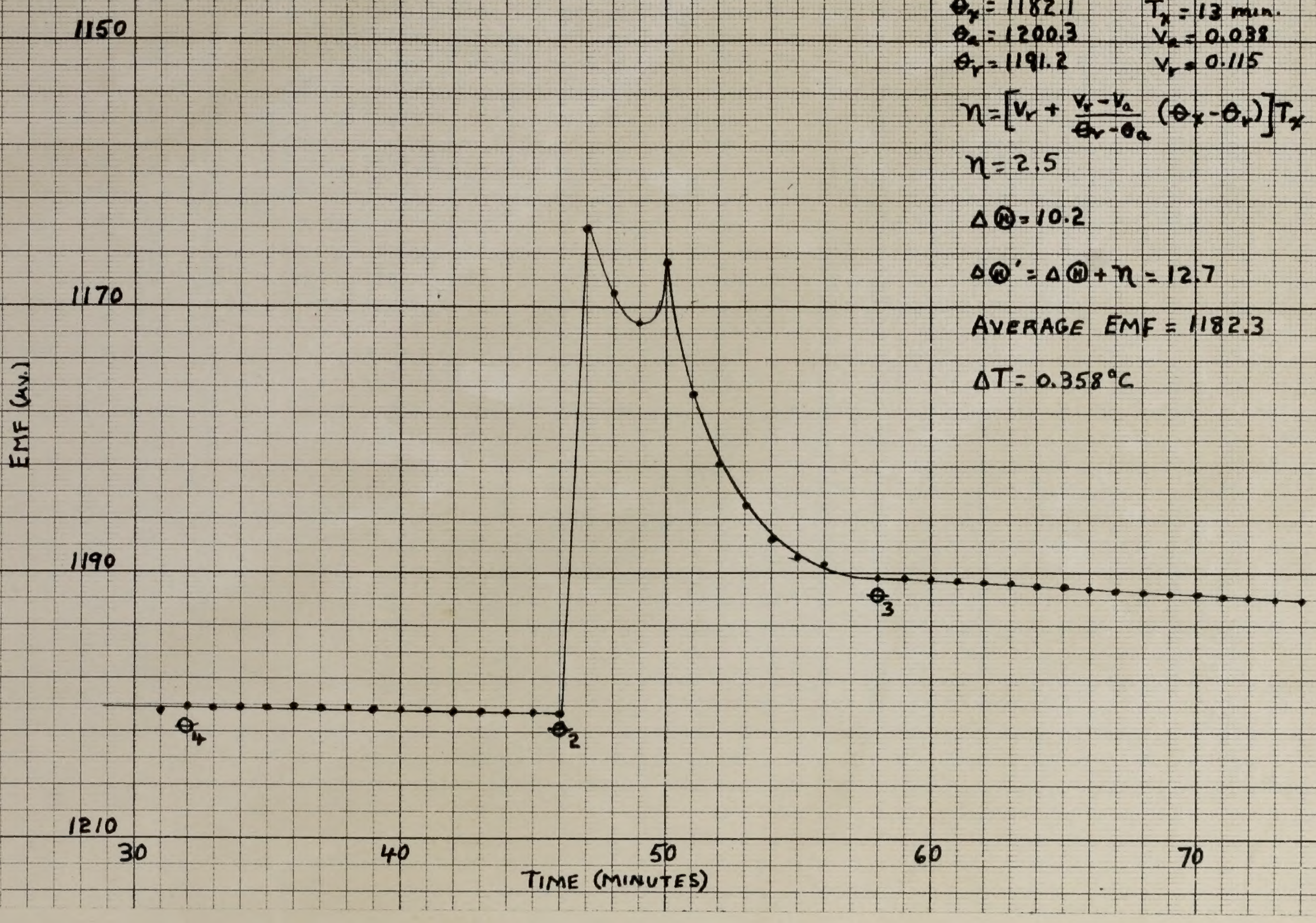
$\Delta\Theta = 15.2$

$\Delta\Theta' = \Delta\Theta + \eta = 17.9$

AVERAGE EMF = 12076

$\Delta T = -0.507$ °C

FIG. 15



TEMPERATURE PATTERN
HEAT OF SOLUTION OF
AMMONIUM BROMIDE

$\theta_x = 1182.1$ $T_x = 13$ min.
$\theta_a = 1200.3$ $V_a = 0.038$
$\theta_r = 1191.2$ $V_r = 0.115$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a} (\theta_x - \theta_r) \right] T_x$$

$\eta = 2.5$

$\Delta \textcircled{H} = 10.2$

$\Delta \textcircled{H}' = \Delta \textcircled{H} + \eta = 12.7$

AVERAGE EMF = 1182.3

$\Delta T = 0.358$ °C

difference of the final and initial temperatures of the reaction period. To this is added the temperature change due to the thermal leakage of the calorimeter, η . The value, η is calculated using an improved form of the Regnault-Pfundler equation

$$(4) \quad \eta = \left[V_r + \frac{V_r - V_a}{\phi_r - \phi_a} (\phi_x - \phi_r) \right] T_x$$

where V_a and V_r (in uv./minute) are the rate of change of the temperature in the periods preceding and following the reaction period, respectively; ϕ_a, ϕ_x, ϕ_r (in microvolts) are the mean temperatures observed during the three periods, and T_x (in minutes) is the length of time of the reaction period. The actual temperature change, $\Delta\Theta'$, is:

$$(5) \quad \Delta\Theta' = \Delta\Theta + \eta$$

where $\Delta\Theta'$ is expressed in microvolts.

The first step in the construction of the temperature pattern is the conversion of the potentiometer scale readings to the corresponding thermocouple EMF's.

The sensitivity of the potentiometer is determined using equation (6)

$$(6) \quad S = \frac{R_B - (R_A + \Delta R)}{P_B - P_A}$$

where S is the sensitivity (number of scale divisions per microvolt), R_A and R_B are consecutive scale readings, ΔR is the mean scale reading change over a period prior to R_A, and P_B and P_A are the potentiometer settings.

The sensitivity determined from the above equation is substituted in equation (7) where the galvanometer scale readings are changed to thermocouple EMF's.

$$(7) \qquad E = P + \frac{R_0 - R}{S}$$

E is the thermocouple EMF, P the potentiometer setting, R_0 the scale reading with the circuit open, R is the scale reading with the circuit closed, and S is the sensitivity.

Since $\Delta \text{Ⓦ}'$ is in microvolts and the temperature change is desired in degrees centigrade, the value of $\Delta \text{Ⓦ}'$ must be divided by a value of dE/dT (Table 35) at the mean reaction temperature.

B. Calculation of the Heat Capacity of the Calorimeter and Its Contents

The total heat capacity of the system is the sum of several individual heat capacities. They are the heat capacities of the ammonium salt, the ammonia in the calorimeter, the calcium metal used, the platinum stirrup, and all glass immersed in the liquid (this includes the submerged portion of the thermocouple, the stirrer, sample crushing rod, and calorimeter walls).

The heat capacities of the ammonium salt and of the calcium metal are determined by multiplication of their respective specific heats (taken from the literature) by the weight of each used.

The contribution to the total heat capacity of the system by the platinum stirrup and glassware (excluding the

calorimeter walls) is determined similarly.

The heat capacity of the calorimeter walls has been determined as a function of the height of the liquid level[9] and has been found to vary in a linear manner (Figure 19). The liquid level height is determined from cathetometer readings of the meniscus of the liquid and of a reference mark. The reference mark is a known distance from the bottom of the calorimeter. The heat capacity of the calorimeter corresponding to any particular liquid height can be read directly from the plot of Heat Capacity vs. Liquid Height (Figure 19).

The heat capacity of the liquid ammonia in the calorimeter is the product of the specific heat of the ammonia at the mean temperature of the reaction period and the weight of ammonia in the calorimeter.

The specific heats of liquid ammonia at temperatures around its boiling point are given in Table 17.[22]

Table 17

HEAT CAPACITY OF LIQUID AMMONIA

T° K	C_p (Cal./mole/°T)
229.93	18.02
233.15	18.05
234.76	18.05
238.33	18.12
239.68	
240.5	18.16

---

22. Overstreet and Giauque, J. Am. Chem. Soc. 59, 254 (1937)

Table 17 (cont.)

Interpolated:

T^o K	C_p (Cal./mole/^oT)	Calculated specific heat (Cal./g/^{o}C.)
239.1 (-34^{o}C)	18.14	1.065
240.1 (-33^{o}C)	18.13	1.065
241.1 (-32^{o}C)	18.12	1.064

The weight of ammonia in the calorimeter is calculated by subtracting from the weight of ammonia condensed into the calorimeter the weight of ammonia vaporized prior to the reaction and one-half the weight vaporized during the reaction.

C. Calculation of the Molar Heat Effect

The product of the total heat capacity of the system and the change in temperature yields the heat effect associated with the temperature change of the calorimeter and its contents.

The heat effect brought about by the vaporization of ammonia during the reaction period is calculated by multiplication of the weight of ammonia vaporized and the heat of vaporization of liquid ammonia at the mean reaction temperature. It has been assumed that the specific heat of vaporization of the liquid ammonia solutions is the same as the heat of vaporization of pure liquid ammonia. The variation of the heat of vaporization with temperature is shown in Table 18.[23]

[23] Osborne and Van Dusen, Bur. Stand. Bull. 14, 439 (1917) or J. Am. Chem. Soc. 40, 14 (1918)

Table 18

HEAT OF VAPORIZATION OF LIQUID AMMONIA

Data from Ref. 23		Interpolated values	
T°C	H (joules)	T°C	H(cal./g)
-35.0	1373	-34	327.6
-33.4	1369	-33	326.9
-30.0	1359	-32	326.2
-25.0	1344	-31	325.5

The weight of ammonia vaporized is calculated using Berthelot's equation of state:

$$(8) \quad PV = n\,R\,T\left[1 + \frac{9\,P\,T_c}{128 P_c T}\left(1 - 6\,\frac{T_c^2}{T^2}\right)\right]$$

Inserting the values of the critical constants we have equation (9)

$$(9) \quad g = \frac{PV}{1 - 0.00828P} \quad (0.0006964)$$

where g is the weight of ammonia vaporized, P is the pressure in atmospheres of the ammonia collected in the gas-collecting system, and V is the volume of the gas-collecting system. Since in a heat of reaction determination both hydrogen and ammonia are vaporized, we must assume the applicability of both Dalton's Law of Partial Pressures and the Ideal Gas Law. In view of the low pressures involved these assumptions appear to introduce only negligible errors. Using Dalton's Law, the pressure of ammonia collected is calculated as the total pressure of gas (ammonia and hydrogen) collected less the pressure exerted by the hydrogen gas. The pressure of hydrogen is determined by use of the ideal gas PV=nRT where n, the

number of moles of hydrogen, is equal to the number of gram-atoms of calcium participating in the reaction.

It is necessary to correct for slight differences in the line pressure of the calorimeter before and after the reaction. The weight of ammonia in the line at each pressure is calculated using equation (9). A value of 800 ml. is substituted for V in equation (9). This value includes the volume of all the glass line plus one-half the volume of the calorimeter above the liquid level. A rough estimate of the additional amount of ammonia vaporized is one milligram per millimeter increase in line pressure.

The total heat effect produced by the reaction of calcium metal in liquid ammonia can now be determined by addition of the heat effects calculated from (1) Δ T x Total Heat Capacity and (2) Weight of ammonia vaporized x heat of vaporization. Dividing the total heat effect associated with the reaction by the number of gram-atoms of calcium taking part in the reaction yields the heat of solution or reaction per gram-atom of metal.

Since the calcium used was found to be impure several of the experiments were followed by an analysis of the contents of the calorimeter, and the total heat effect was corrected for the amount of the sample which actually participated in the reaction as calcium metal.

Assuming the impurity to be only calcium oxide, a calculation was made (using the percent of the oxygen present

in the sample, the atomic weight of calcium, and the molecular weight of calcium oxide) to determine the weight of calcium oxide present.

A value of 30,000 cal./gm-atom was used for the heat effect produced by the reaction of calcium oxide with ammonium ion in liquid ammonia. Since the heat of reaction of the alkali metals with ammonium ion in liquid ammonia is approximately two-thirds the heat effect associated with the similar reaction with H_3O^+ in water, it was assumed that the heat of reaction of calcium oxide with ammonium ion in liquid ammonia would be two-thirds of the heat effect produced by the reaction of calcium oxide with hydrogen ion in the water. The value for the heat of reaction of calcium oxide in the aqueous system was determined from heat of formation data. The heat effect associated with the reaction of calcium oxide with the ammonium ion in liquid ammonia is less than three percent of the total heat effect produced during the experiment. Therefore it appears that any error introduced by the assumptions involved in determining the value of 30,000 calories would be very small.

Multiplication of the number of gram-atoms of calcium oxide present by the heat of reaction value (30,000 calories) produced the heat effect associated with that many gram-atoms of calcium oxide reacting in liquid ammonia.

The number of gram-atoms of calcium involved in the reaction, and therefore the number moles of hydrogen evolved

during the reaction was now different than had originally been thought. This necessitated the redetermination of the weight of ammonia collected in the gas-collecting system, and a recalculation of the heat effect produced by the vaporization of this new weight of ammonia.

The total heat effect produced in the reaction was the sum of the heat effects associated with (1) the temperature change of the calorimeter and its contents, and (2) the vaporization of the corrected weight of ammonia. Subtracting from this sum the heat effect associated with the reaction of solid calcium oxide with ammonium ion in liquid ammonia yielded the heat effect associated with the reaction of calcium metal only. Dividing this value by the number gram-atoms of calcium actually involved in the reaction yielded a new value for the heat of reaction of calcium metal with ammonium ion in liquid ammonia.

Quantitative tests showed calcium oxide to be insoluble in liquid ammonia. Therefore the only correction necessary in heat of solution calculations was in the actual number of gram-atoms of calcium going into solution. The total heat effect remained the same. The heat of solution was recalculated by dividing the total heat effect by the number of grams of calcium going into solution.

A detailed sample calculation is presented in Table 19.

TABLE 19

SAMPLE CALCULATION OF THE HEAT OF REACTION, ΔH_2, FOR EXPERIMENT 4

A. Temperature Change

1. Temperature pattern

$$S = \frac{R_B - (R_A + \Delta R)}{P_B - P_A}$$

at t = 36 minutes

$$S = \frac{46.9 - (51.5 \quad 0.2)}{1200 - 1199} = -4.8 \text{ scale div./uv.}$$

From equation (7)

$$E = P + \frac{R_0 - R}{S}$$

$$E = 1200 + \frac{49.9 - 46.9}{-4.8} \doteq 1199.4 \text{ uv.}$$

Substitution in equation (7) of the values P, R_0, R, and S for each minute interval yields the corresponding values of E. They are tabulated as shown:

Time	P	R	E
36	1200	46.9	1199.4
37	1200	46.9	1199.4
38	1200	47.0	1199.4

where the time is in minutes, P is the potentiometer setting in microvolts, R is the galvanometer scale reading, and E is the EMF in microvolts. These values are plotted to obtain the temperature pattern of the experiment.

$\Delta\Theta'$ is obtained as the sum of $\Delta\Theta$ and η

$\Delta\Theta$ = the difference between the final and intial temperatures of the reaction period = 19.5 uv.

η is obtained using the modified form of the Regnault-Pfundler equation.

$$\eta = \left[V_r + \frac{V_r - V_a}{\phi_r - \phi_a} \left(\phi_x - \phi_r \right) \right] T_x$$

For this experiment η = 1.2 uv.

$\Delta\Theta' = 19.5 + 1.2 = 20.7$ uv.

$\Delta\Theta'$ is now converted to temperature in degrees centigrade.

At the mean EMF (1218.1 uv.)

$$dE/dT = 35.33 \text{ uv.}/^\circ C$$

$$\Delta T = \frac{\quad}{dE/dT} = \frac{-20.7}{35.33} \stackrel{*}{=} -0.586 \ ^\circ C$$

B. Heat Capacity of System

Ammonia vaporized prior to the reaction

$$g = \frac{PV \ (0.0006964)}{1 - 0.00828 \ P}$$

$$g = \frac{(33.7/760) \ (6715) \ (0.0006964)}{1 - 0.00828 \ (33.7/760)} = 0.2074 \ g$$

The heat capacity of the system is the sum of the individual heat capacities involved. The manner in which the individual heat capacities are determined is indicated in Table 20.

C. Heat Effect

1. The heat effect associated with the temperature change of the calorimeter and its contents:

   ΔT x Heat capacity of system = -0.586 x 145.3 = -85.2 cal.

2. Heat of vaporization

   a. Moles hydrogen evolved = gram-atoms Ca = 0.000938

   b. Mm. of hydrogen collected

   $$PV = nRT$$

$$P = \frac{(0.000938)\ (82.05)\ (298)}{6715} = 2.60 \text{ mm.}$$

c. Mm. of ammonia collected

Total pressure ammonia and hydrogen	85.80 mm
pressure hydrogen	2.60
pressure ammonia	83.20 mm

d. Weight ammonia evolved

Substituting in equation (9)

$$g = \frac{(83.20/760)\ (6715)\ (0.0006964)}{1 - 0.00828\ (83.20/760)} = 0.5124 \text{ g}$$

e. No line pressure correction (It would be calculated using equation (9) where V= 800 ml.)

f. The heat effect associated with the vaporization of ammonia

Wt. ammonia vaporized x Heat of vaporization per gram at mean reaction temperature

0.5124 x 326.9 = 167.5 cal.

3. Total Heat effect = 167.5 - 85.2 = 81.5 cal.

This is the heat effect associated with the reaction of calcium with the ammonium ion, therefore

$$\Delta H_2 = \frac{81.5 \text{ cal.}}{0.000938} = 87{,}700 \text{ cal. per gram-atom}$$

D. Analysis of Calorimeter Contents

Titration with potassium permanganate showed 91.2% of the sample weight to be calcium. Assuming the remaining 8.8% to be oxygen the percent of calcium oxide was determined.

$$\frac{\text{Molecular Wt. calcium oxide}}{\text{Atomic Wt. oxygen}} \times \%\ \text{oxygen} = \%\ \text{calcium oxide}$$

$\frac{56}{16} \times 8.8 = 28.7\%$ calcium oxide

Therefore there was 81.3% of the sample present as calcium metal.

1. Wt. of calcium present = Wt. of sample x % calcimm metal

   0.0376 x .813 = 0.0305 grams

2. Wt. of calcium oxide present = 0.0376 - 0.0305

   = 0.0071 grams calcium oxide or 0.000127 gram-atoms

E. Corrected Data

1. Since the weight of calcium metal present has changed, the number of moles of hydrogen evolved must also have changed. Using the Ideal Gas Law, as before, where n is the new number of gram-atoms of calcium

   $P_{hydrogen} = 2.10$ mm.

   $P_{ammonia} = 83.70$ mm

2. From equation (9) the weight of ammonia vaporized is found to equal 0.5115 grams.

3. The heat effect associated with the new weight of ammonia vaporized equals 168.5 cal.

4. Total heat effect = 168.5 - 85.2 = 83.3 cal.

5. Heat effect due to reaction of 0.000127 moles of calcium oxide with ammonium ion

   0.000127 x 30,000 cal. = 3.8 cal.

   The heat of reaction per mole is assumed to be 30,000 calories.

6. Corrected heat effect

$$83.3 - 3.8 = 79.5 \text{ cal.}$$

7. Corrected heat of reaction per gram-atom of calcium metal.

$$79.5 \text{ cal.}/\ 0.000761 = -105{,}500 \text{ calories}$$

TABLE 20

SUMMARY OF CALCULATIONS
EXPERIMENT A

A. Temperature Change

Average E (from temperature pattern)	1191.6 uv.
Average T (from Table 35)	-32.24 °C
dE/dT , (Table 35)	-35.33 uv/°C
Δ E (ΔⒺ)	4.1 uv
Δ T	0.116 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.4025	0.15	0.1
3. Calorimeter (from fig. 19 for liquid height of 153.7 mm.)			22.1
4. Ammonia in calorimeter:			
weighed in	121.31		
vaporized prior to reaction	1.05		
½ amount vaporized during reaction	0.34		
	119.92	1.064	127.7

Total Heat Capacity of System 151.1

C. Heat Effect

1. ΔT x Heat capacity of system = 0.116 x 151.1 17.5 cal.
2. Heat of vaporization:
   - a. Volume of gas-collecting system 6715 ml.
   - b. Mm of ammonia collected 109.2 mm
   - c. Wt. of ammonia vaporized 0.6730 g
     line pressure correction 0.0033
     0.6763 g
   - . Wt. ammonia x heat of vaporization per gram (Table 18) = 0.6763 x 326.4 cal./g 220.6
3. Total heat effect = 17.5 + 220.6 238.1
4. Heat of solution per gram-atom calcium
   238.1 cal/0.0100 = ΔH_1 = -23,800 cal.

D. Dilution Ratio - 760 moles NH_3/ gram-atom calcium

TABLE 21

SUMMARY OF CALCULATIONS
EXPERIMENT B

A. Temperature Change

Average E (from temperature pattern)	1201.0 uv.
Average T (from Table 35)	-32.53 °C
dE/dT , (Table 35)	-35.33 uv/°C
Δ E (ΔⒽ)	12.2 uv
Δ T	0.346 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.4248	0.15	0.1
3. Calorimeter (from fig.19 for liquid height of 139.1 mm.)			18.8
4. Ammonia in calorimeter			
weighed in:	110.98		
vaporized prior to reaction	1.77		
½ amount vaporized during reaction	0.36		
	108.85	1.064	115.8

Total Heat Capacity of System 135.9

C. Heat Effect

1. ΔT x Heat capacity of system = 0.346 x 135.9 47.0 cal.
2. Heat of vaporization
   - a. Volume of gas-collecting system 6715 ml.
   - b. Mm of ammonia collected 117.10 mm.
   - c. Wt. of ammonia vaporized 0.7215 g
     - line pressure correction 0.0028
     - 0.7243 g
   - d. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.7243 x 326.5 cal/g 236.5
3. Total heat effect = 47.0+ 236.5 283.5
4. Heat of solution per gram-atom calcium
   283.5 cal./0.0106 = ΔH_1 =-26,800 cal.

D. Dilution Ratio - 615 moles NH_3/ gram-atom calcium

TABLE 22

SUMMARY OF CALCULATIONS
EXPERIMENT C

A. Temperature Change

Average E (from temperature pattern)	1211.1 uv.
Average T (from Table 35)	-32.78°C
dE/dT , (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ')	2.8 uv
ΔT	-0.079°C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.2139	0.15	0.1
3. Calorimeter (from fig. 19 for liquid height of 144.7 mm.)			20.0
4. Ammonia in calorimeter			
weighed in:	112.33		
vaporized prior to reaction	0.55		
½ amount vaporized during reaction	0.18		
	111.60	1.064	118.7

Total Heat Capacity of System 140.0

C. Heat Effect

1. ΔT x Heat capacity of system = -0.079 x 140.0 -11.1 cal.
2. Heat of vaporization
   - a. Volume of gas-collecting system 6715 ml.
   - b. Mm of ammonia collected 60.70 mm
   - c. Wt. of ammonia vaporized 0.3728 g
     line pressure correction - 0.0013
     0.3715
   - d. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.3715 x 326.8 cal/g 121.6
3. Total heat effect = 121.6 - 11.1 110.5
4. Heat of solution per gram-atom calcium
   110.5 cal/0.00544 = ΔH_1 = -20,400 cal.

D. Dilution Ratio - 1215 moles NH_3/ gram-atom Ca

TABLE 23

SUMMARY OF CALCULATIONS
EXPERIMENT D

A. Temperature Change

Average E (from temperature pattern)	1199.4 uv
Average T (from Table 35)	$-32.46^{\circ}C$
dE/dT (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ')	2.9 uv
ΔT	-0.082 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.1759	0.15	0.1
3. Calorimeter (from fig. 19 for liquid height of 135.7 mm)			18.0
4. Ammonia in calorimeter			
weighed in	103.90		
vaporized prior to reaction	0.40		
½ amount vaporized during reaction	0.17		
	103.33	1.064	110.0

Total Heat Capacity of System 129.3

C. Heat Effect

1. ΔT x Heat capacity of system = -0.082×128.2 -10.6 cal.
2. Heat of vaporization
   a. Volume of gas-collecting system 6715 ml.
   b. Mm of ammonia collected 54.90 mm
   c. Wt. of ammonia vaporized 0.3380 g
      line pressure correction 0.0040
      0.3420
   d. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.3420×326.6 cal/g 111.7
3. Total heat effect = $111.7 - 10.6$ 101.1
4. Heat of solution per gram-atom calcium
   101.1 cal/0.00440 = $\Delta H_1 = -23{,}000$ cal.

D. Dilution Ratio - 1390 moles NH_3/gram-atom calcium

TABLE 24

SUMMARY OF CALCULATIONS
EXPERIMENT E

A. Temperature Change

Average E (from temperature pattern)	1201.5 uv
Average T (from Table 35)	-32.52°C
dE/dT (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ)	11.7 uv
ΔT	0.332 °C

B. Heat Capacity of System

Item	Weight(g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.1998	0.15	0.1
3. Calorimeter (from fig. 19 for liquid height of 152.7 mm)			21.9
4. Ammonia in calorimeter			
weighed in	121.16		
vaporized prior to reaction	0.27		
½ amount vaporized during reaction	0.10		
	120.79	1.064	128.5

Total Heat Capacity of System 151.7

C. Heat Effect

1. ΔT x Heat capacity of system = 0.332 x 151.7 50.4 cal.
2. Heat of vaporization
   - a. Volume of gas-collecting system 6715 ml.
   - b. Mm of ammonia collected 30.2 mm
   - c. Wt. of ammonia vaporized 0.1859 g
     line pressure correction 0.0088
     0.1947 g
   - d. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.1947 x 326.6 cal/g 63.6
3. Total heat effect = 50.4 + 63.6 114.0
4. Heat of solution per gram-atom calcium
   114.0 cal/0.0050 = ΔH_1 = -22,800 cal.

D. Dilution Ration - 1430 moles NH_3/gram-atom calcium

TABLE 25

SUMMARY OF CALCULATIONS
EXPERIMENT F

A. Temperature Change

Average E (from temperature pattern)	1200.0 uv.
Average T (Table 35)	-32.47 °C
dE/dT (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ$'$)	5.1 uv
ΔT	-0.144 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.1814	0.15	0.1
3. Calorimeter (from fig. 19 for liquid height of 143.9 mm)			19.9
4. Ammonia in calorimeter			
weighed in	117.71 g		
vaporized prior to reaction	0.26		
½ amount vaporized during reaction	0.17	1.064	118.4
Total Heat Capacity of System			139.6

C. Heat Effect

1. ΔT x Heat capacity of system = -0.144 x 139.6 -20.1
2. Heat of vaporization
   a. Volume of gas-collecting system 6715 ml.
   b. Mm of ammonia collected 54.8 mm
   c. Wt. of ammonia vaporized 0.3392 g
      line pressure correction -0.0035
      0.3367
   d. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.3367 x 326.6 cal/g 110.0
3. Total heat effect = 110.0 - 20.1 89.7
4. Heat of solution per gram-atom calcium
   89.7 cal/0.00452 = -19,900 cal.

D. Analysis of Calorimeter Contents

TABLE 25 (continued)

1. Wt. of calcium present 0.1747 g
2. Wt. of calcium oxide present 0.0235 g
3. Wt. of calcium metal 0.1579 g
4. Gram-atoms calcium metal 0.00395
5. Corrected heat of solution per gram-atom calcium
   89.7 cal/0/00395 = ΔH_1 = -22,800 cal.

E. Dilution Ratio - 1660 moles NH_3/ gram-atom calcium

TABLE 26

SUMMARY OF CALCULATIONS
EXPERIMENT G

A. Temperature Change

Average E (from temperature pattern)	1198.8 uv.
Average T (from Table 35)	-32.44 °C
dE/dT (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ')	3.5 uv
ΔT	-0.099 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.1945	0.15	0.1
3. Calorimeter (from Fig. 19 for liquid height of 141.3 mm)			19.3
4. Ammonia in calorimeter			
weighed in	110.44		
vaporized prior to reaction	0.40		
½ amount vaporized during reaction	0.17		
	109.87	1.064	116.9

Total Heat Capacity of System 137.5

C. Heat Effect

1. ΔT x Heat capacity of system = -0.099 x 137.5 -13.6 cal.
2. Heat of vaporization
    - a. Volume of gas-collecting system 6715 ml.
    - b. Mm of ammonia collected 54.6 mm
    - c. Wt. of ammonia vaporized 0.3362 g
      line pressure correction 0.0013
      0.3375 g
    - d. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.3375 x 326.6 cal/g 110.2
3. Total heat effect = 110.2 - 13.6 96.6
4. Heat of solution per gram-atom calcium
   96.6 cal/ 0.00485 = -19,900 cal.

D. Analysis of Calorimeter Contents

1.	Wt. of calcium present	0.1895 g
2.	Wt. of calcium oxide present	0.0171 g
3.	Wt. of calcium metal	0.1774 g
4.	Gram-atoms of calcium metal	0.00443

5. Corrected heat of solution per gram-atom calcium
$$96.6 \text{ cal.} / 0.00443 = \Delta H_1 = -21{,}900 \text{ cal.}$$

E. Dilution Ratio - 1470 moles NH_3/ gram-atom calcium

TABLE 27

SUMMARY OF CALCULATIONS
EXPERIMENT 1

A. Temperature Change

Average E (from temperature pattern)	1211.9 uv
Average T (from Table 35)	-32.81°C
dE/dT (Table 35)	-35.33 uv/°C
ΔE (Δω)	20.6 uv
ΔT	-0.584 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.0421	0.15	0.0
3. Ammonium iodide	0.3469	0.1	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (from fig. 19 for liquid height of 145.5 mm)			20.2
6. Ammonia in calorimeter			
weighed in	116.45		
vaporized prior to reaction	0.15		
½ amount vaporized during reaction	0.25		
	116.05	1.064	123.5

Total Heat Capacity of System 145.1

C. Heat Effect

1. ΔT x Heat capacity of system = -0.584 x 145.1 -84.7
2. Heat of vaporization
   - a. Volume of gas-collecting system 6715 ml.
   - b. Total mm. gas collected 84.5 mm
   - c. Moles of hydrogen evolved 0.00105
   - d. Mm of hydrogen collected 2.9 mm
   - e. Mm of ammonia collected 81.6 mm
   - f. Wt. ammonia vaporized 0.5026 g
     No line pressure correction
   - g. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.5026 x 326.8 cal/g 164.2

3. Total heat effect = 164.2 - 84.7 79.5
4. Heat of Reaction per gram-atom calcium
$79.5 \text{ cal.}/0.00105 = \Delta H_2 = -75{,}700 \text{ cal.}$

TABLE 28

SUMMARY OF CALCULATIONS
EXPERIMENT 2

A. Temperature Change

Average E (from temperature pattern)	1202.7 uv
Average T (from Table 35)	-32.55 °C
dE/dT (Table 35)	-35.33 uv/°C
ΔE ($\Delta\textcircled{H}'$)	2.1 uv
ΔT	-0.059 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.0400	0.15	0.0
3. Ammonium iodide	0.3200	0.1	0.0
4. Platinum	6.4	0.03	0.2
5. Calorimeter (from fig. 19 for liquid height of 145.8 mm)			20.3
6. Ammonia in calorimeter			
weighed in	115.68		
vaporized prior to reaction	0.17		
½ amount vaporized during reaction	0.14		
	115.37	1.064	122.8

Total Heat Capacity of System 144.5

C. Heat Effect

1. ΔT x Heat Capacity of system = -0.059 x 144.5 -8.5 cal.
2. Heat of vaporization

a. Volume of gas-collecting system	6715 ml.
b. Total mm. gas collected	48.95 mm
c. Moles of hydrogen evolved	0.0010
d. Mm of hydrogen collected	2.77 mm
e. Mm of ammonia collected	46.18 mm
f. Wt. NH_3 vaporized	0.2843 g
line pressure correction	0.0008
	0.2851

g. Wt. ammonia vaporized x Heat of vaporization per gram(Table 18) = 0.2851 x 326.6 cal/g 93.1

3. Total Heat effect = 93.1 - 8.5 84.6

4. Heat of reaction per gram-atom calcium

84.6 cal/ 0.0010 = ΔH_2 = -84,600 cal.

TABLE 29

SUMMARY OF CALCULATIONS
EXPERIMENT 3

A. Temperature Change

Average E (from temperature pattern)	1210.1 uv
Average T (from Table 35)	-32.77 °C
dE/dT (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ)	20.8 uv
ΔT	-0.589°C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.0380	0.15	0.0
3. Ammonium iodide	0.3621	0.1	0.0
4 Platinum	6.4	0.03	0.2
5. Calorimeter (from fig. 19 for liquid height of 145.8 mm)			20.5
6. Ammonia in calorimeter			
weighed in	116.73		
vaporized prior to reaction	0.35		
½ amount vaporized during reaction	0.27		
	116.11	1.064	123.5

Total Heat Capacity of System 145.4

C. Heat Effect

1. ΔT x Heat capacity of system = -0.589 x 145.4 -85.6 cal.
2. Heat of vaporization

a. Volume of gas-collecting system	6715 ml.
b. Total mm gas collected	89.65 mm
c. Moles of hydrogen evolved	0.00095
d. Mm of hydrogen collected	2.63 mm
e. Mm of ammonia collected	87.02 mm
f. Wt. ammonia vaporized	0.5360 g
line pressure correction	-0.0008
	0.5352

g. Wt. ammonia x Heat pf vaporization per gram (Table 18) = 0.5352 x 326.8 cal/g 174.9 cal.

3. Total heat effect = 174.9 - 85.6 89.3
4. Heat of reaction per gram-atom calcium
$89.3 \text{ cal}/ 0.00095 = \Delta H_2 = -94{,}000 \text{ cal.}$

TABLE 30

SUMMARY OF CALCULATIONS
EXPERIMENT 4

A. Temperature Change

Average E (from temperature pattern)	1209.5 uv
Average T (from Table 35)	-32.74 °C
dE/dT , (Table 35)	-35.33 uv/°C
ΔE (ΔⒽ′)	20.7 uv
ΔT	-0.586 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.0376	0.15	0.0
3. Ammonium iodide	0.3581	0.1	0.0
4. Platinum	8.0	0.03	0.2
5 Calorimeter (from fig. 19 for liquid height of 145.5 mm			20.3
6. Ammonia in calorimeter			
weighed in	116.64		
vaporized prior to reaction	0.21		
½ amount vaporized during reaction	0.26	1.064	123.6
Total Heat Capacity of System			145.3

C. Heat Effect

1. ΔT x Heat capacity of system = -0.586 x 145.3		-85.2 cal.
2. Heat of vaporization		
a. Volume of gas-collecting system	6715 ml.	
b. Total mm gas collected	89.1 mm	
c. Moles hydrogen evolved	0.000938	
d. Mm of hydrogen collected	2.60mm	
e. Mm of ammonia collected	83.20 mm	
f. Wt. ammonia vaporized no line pressure correction	0.5124 g	
g. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.5124 x 326.9 cal/g		167.5
3. Total heat effect = 167.5 - 85.2		82.3

4. Heat of reaction per gram-atom calcium
   82.3 cal/ 0.000938 = -87,700 cal.

D. Analysis of Calorimeter Contents

1. Wt. of calcium present	0.0343 g
2. Wt. of calcium oxide present	0.0071 g
3. Wt. of calcium metal	0.0305 g
4. Gram-atoms of calcium metal	0.000761

E. Corrected Data

1. Moles of hydrogen evolved	0.000761	
2. Mm of hydrogen collected	2.10 mm	
3. Total mm. of gas collected	85.80 mm	
4. Mm ammonia collected	83.70 mm	
5. Wt. ammonia vaporized	0.5115 g	
No line pressure correction		
6. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.5115 x 326.9 cal/g		168.5 cal.
7. Total heat effect = 168.5 - 85.2		83.3
8. Heat effect due to reaction of calcium oxide		3.8
9. Corrected heat effect = 83.3 - 3.8		79.5

10. Heat of reaction per gram-atom calcium
   79.5 cal/ 0.000761 = ΔH_2 = -105,500 cal.

TABLE 31 SUMMARY OF CALCULATIONS
EXPERIMENT 5

A. Temperature Change

Average E (from temperature pattern)	1207.6 uv.
Average T (from Table 35)	-32.69°C
dE/dT (Table 35)	-35.33 uv/°C
ΔE ($\Delta\Theta'$)	17.9 uv
ΔT	-0.507 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6	0.2	1.2
2. Calcium	0.0396	0.15	0.0
3. Ammonium iodide	0.3200	0.1	0.0
4. Platinum	8.0	0.03	0.2
5. Calorimeter (from fig. 19 for liquid height of 144.8 mm.			20.1
6. Ammonia in calorimeter			
weighed in	116.82		
vaporized prior to reaction	0.35		
½ amount vaporized during reaction	0.26		
	116.21	1.064	123.6

Total Heat Capacity of System 145.1

C. Heat Effect

1. ΔT x Heat capacity of system = -0.507 x 145.1 -73.6 cal.
2. Heat of vaporization

a. Volume of gas-collecting system	6715 ml.
b. Total mm. gas collected	89.10 mm
c. Moles hydrogen evolved	0.000987
d. Mm of hydrogen collected	2.73 mm
e Mm of ammonia collected	86.37 mm
f. Wt. ammonia vaporized	0.5320 g
line pressure correction	0.0010
	0.5330 g

g. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.5330 x 326.8 cal./g 174.2

3. Total heat effect = 174.2 - 73.6 100.6 cal.
4. Heat of reaction per gram-atom calcium
   100.6 cal/ 0.000987 = -101,900 cal.

D. Analysis of Calorimeter Contents

1. Wt. of calcium present	0.0388 g
2. Wt. of calcium oxide present	0.0028 g
3. Wt. of calcium metal	0.0368 g
4. Gram-atoms of calcium metal	0.000918

E. Corrected Data

1. Moles of hydrogen evolved	0.000918	
2. Mm of hydrogen collected	2.54 mm	
3. Total mm gas collected	89.10 mm	
4. Mm ammonia collected	86.56 mm	
5. Wt. of ammonia vaporized	0.5332 g	
line pressure correction	0.0010	
	0.5342 g	
6. Wt. ammonia x Heat of vaporization per gram (Table 18) = 0.5342 x 326.8 cal/g		174.6
7. Total heat effect = 174.6 - 73.6		101.0
8. Heat effect due to reaction of calcium oxide		1.5
9. Corrected heat effect = 101.0 - 1.5		99.5

10. Heat of reaction per gram-atom calcium
    99.5 cal/ 0.000918 = ΔH_2 = -108,400 cal.

TABLE 32 SUMMARY OF CALCULATIONS
DETERMINATION OF THE HEAT OF SOLUTION OF AMMONIUM BROMIDE

A. Temperature Change

Average E (from temperature pattern)	1182.3 uv.
Average T (from Table 35)	-31.97°C
dE/dT	-35.48 uv/°C
ΔE (ΔⒽ)	12.7 uv
ΔT	0.358 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat (cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	6.5	0.2	1.3
2. Ammonium bromide	4.2935	0.21	0.9
3. Calorimeter (from fig. 19 for liquid height of 141.5 mm)			19.3
4. Ammonia in calorimeter			
weighed in	113.40		
vaporized prior to reaction	0.44		
½ amount vaporized during reaction	0.55		
	112.41	1.064	119.60

Total Heat Capacity of System 141.1

C. Heat Effect

1. ΔT x Heat capacity of system = 0.358 x 141.1 50.5 cal.
2. Heat of vaporization
   - a. Volume of gas-collecting system 6715 ml.
   - b. Mm of ammonia collected 177.70 mm
   - c. Wt. ammonia vaporized 1.096 g
   - c'. line pressure correction 0.004
   - 1.100 g
   - d. Wt. ammonia x Heat of vaporization per gram(Table 18) = 1.100 x 326.2 358.8
3. Total heat effect = 50.5+ 358.8 409.3

4. Heat of solution per gram -atom ammonium bromide
409.3 cal/ 0.0438 = -9350 cal.

D. Dilution Ratio - 153 moles ammonia/mole ammonium bromide

V. DISCUSSION AND CONCLUSIONS

The first experiments in this research were made to determine the heat of solution of calcium in liquid ammonia. Schmidt[17] had previously determined the heat of solution but in a more concentrated range with the greatest dilution being 366 moles ammonia/ gram-atom calcium. The values obtained were apparently changing rapidly with concentration indicating the necessity of making determinations at greater dilutions. Towards this end experiments A,B, and C were conducted . Plotting the results obtained (figure 16) gave a smooth curve which, however, indicated that the heat of solution had not yet reached a constant value. Therefore experiment D was performed at a still greater dilution.

Since experiment C yielded a value of -20,400 calories at 1216 moles ammonia/gram-atom calcium, a somewhat lower value was anticipated for experiment D where there were 1390 moles ammonia/gram-atom calcium. The result of -23,00 calories was therefore far out of line with that expected on the basis of previous experiments.

During this work, it was also noted that the results of experiments A,B,C, and D disagreed radically with those predicted by the extrapolation of the curve drawn through the heat of solution values obtained by Schmidt. On the basis of Schmidt's work, a heat of solution of approximatel -8000 calories was expected at dilutions of 600-800 moles ammonia/

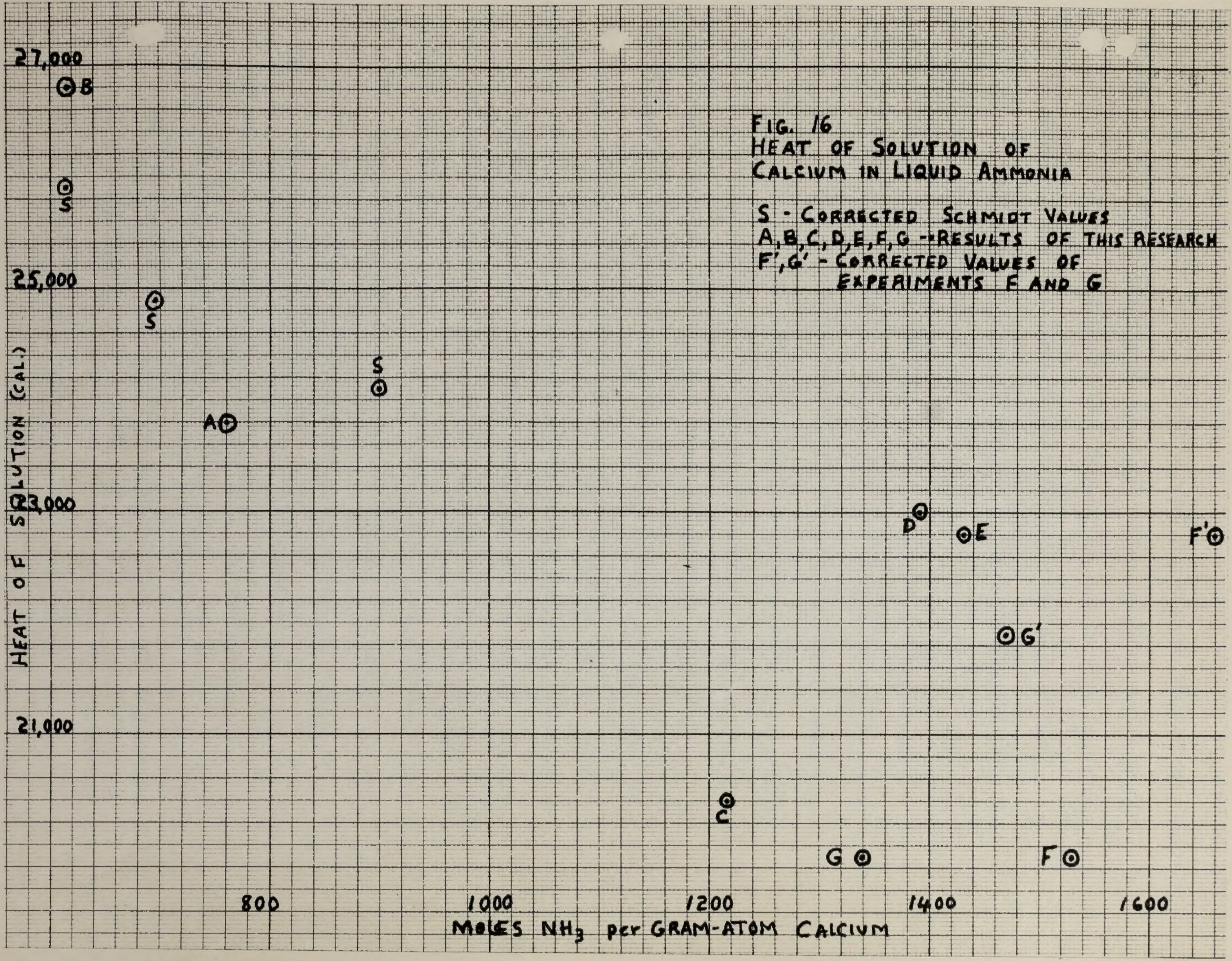


Fig. 16
HEAT OF SOLUTION OF
CALCIUM IN LIQUID AMMONIA

S - CORRECTED SCHMIDT VALUES
A, B, C, D, E, F, G - RESULTS OF THIS RESEARCH
F′, G′ - CORRECTED VALUES OF
EXPERIMENTS F AND G

gram-atom calcium. Experiments A and B yielded values of -23,800 calories at 760 moles ammonia/ gram-atom calcium and -26,800 calories at 615 moles ammonia/ gram-atom calcium respectively. Experiments C and D, though made at greater dilutions, yielded values in the same range as A and B (-20,400 cal. and -23,000cal. respectively).

There were two apparent discrepancies which needed some explanation. First, there was the discrepancy between Schmidt's values and the results obtained in this research, and second, there was the inability to successfully reproduce heat of solution values. No explanation was evident for the first discrepancy, but it was thought that during the investigation of the lack of reproducibility of the heat of solution values some light would also be shed on the large disagreement with the results obtained by Schmidt.

Several sources of error existed which could possibly have influenced the experimental results. They were (1) the effect of light on the liquid ammonia solutions of calcium, (2) the possibility of decomposition of the solution and the formation of the amide, (3) the possiblity of an inherent error in the experimental technique and apparatus, and (4) the purity of the sample which, of course, may be employed to account for any anomaly.

Work on the absorption spectrum of the liquid ammonia solutions of the alkali metals[24] indicated the spectrum to

[24] E. Vogt, Z. Electro chem 45, 597(1939)

be continuous with a peak in the infra-red at about 1.8 μ. Ogg[25] also observed the relatively great infra-red photosensitivity of liquid ammonia solutions of sodium, and he performed photoconductivity measurements that showed the light absorption to be accompanied by the photorelease of electrons. Since the calcium solutions used in experiments A,B,C, and D were exposed to the light, it was possible that absorption of the infra-red was in some manner affecting the nature of the solutions. This necessitated consideration as a possible source of error, and an experimental investigation was undertaken to determine the effect of light absorption on the heat of solution values.

To determine the possible effect of light on the experimental results, temperature measurements were made on a solution of calcium in liquid ammonia under three varied sets of conditions.

(1) The large outer Dewar and the calorimeter were placed with the unsilvered strips aligned, as in the experiments, allowing the light from the windows to enter the calorimeter. Thermocouple readings were made and the solution was observed to be cooling at a rate of 0.09 scale divisions per minute (0.017 uv) or -0.00050°C/minute.

(2) The Dewar was turned so that the unsilvered strips

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[25] Ogg, J. Am. Chem. Soc. 68, 155(1946)

were ninety degrees apart and no light could enter the calorimeter. The windows were covered and the lights in the room were extinguished. Thermocouple readings showed the solution to be cooling at a rate of 0.21 scale divisions per minute (0.041 uv) or -0.0012 °C per minute.

(3) The unsilvered portion of the two Dewars were again aligned, and the contents of the calorimeter exposed to the light of a 60 watt bulb clamped in position 1-2 ft. from the outer Dewar. Temperature readings showed the solution to be warming at a rate of 2.1 scale divisions per minute (0.41 uv) or 0.016°C per minute.

During all of this experiment the conditions, other than the amount of light entering the calorimeter, were identical with those prevailing during an actual heat of solution determination.

The results of the first two parts of the experiment, (1) with light allowed to enter the calorimeter, and (2) with no light allowed to enter the calorimeter, showed only a 0.0007 °C/minute difference in the rate of change of temperature. However, in the third part of the experiment, where an external light source was placed near the calorimeter, a difference of 0.016 °C/minute from parts (1) and (2) was observed in the rate of change of the temperature of the solution. The results of this work indicated that the solutions of calcium in liquid ammonia were affected by light absorption.

An accurate determination was made of the energy

absorbed by calcium solutions due to light absorption during an experiment. A determination of the heat of solution of ammonium bromide in liquid ammonia was made, and the rate of change of temperature after the reaction (V_r) was observed. V_r was found to equal 0.115 uv/minute. Since ammonium bromide solutions were not affected by light, this value of V_r served as the theoretical value which would be expected for calcium solutions were it not for light absorption. A value of 0.038 uv/minute was obtained as the average of the values of V_r in experiments F and G. The difference in the two temperature drifts represented the energy absorbed by the calcium solution because of light falling on the calorimeter. This difference of 0.077 uv/minute corresponded to a temperature difference of 0.0022 °C per minute. Multiplying by an average heat capacity of 140 calories per degree centigrade it was found that 0.3 calories/minute were absorbed by the calcium solution. No correction, however, was made to the heat of solution values since a consideration of the calculations involved in determining the heat of solution indicated that the effect of the energy absorbed was automatically taken care off.

To check the above work a heat of solution determination was performed under conditions where no light (except that which entered from the top of the calorimeter) was allowed to fall on the calorimeter contents. Experiment E was done in such a manner. The windows were covered, the lights in the

room were extinguished, and the unsilvered strips were silvered as well as being placed ninety degrees apart. However, experiment E yielded a value of -22,800 calories at 1430 moles ammonia/gram-atom calcium. This results was in agreement with that obtained from experiment D. The discrepancy with the previous work still existed. It was evident that though light absorption does have some effect upon the solution it could not account for the large disagreement found.

The work turned to the investigation of the second possible source of error, the decomposition of the calcium solution with formation of the amide. The alkali metal solutions of liquid ammonia have been shown to be quite stable but the decomposition has been found to be catalyzed by impurities such as iron and platinum black. If the amide had been formed in experiment D, the heat effect measured would have been the sum of the two heat effects (1) that associated with the solution of the calcium and (2) that associated with the formation of the amide. This would explain the obtaining of a larger value for the heat of solution than expected. However, it is known that the formation of the amide is auto-catalytic. Therefore, if the amide was formed, the experimental measurements would not follow their usual pattern. The evolution of hydrogen as a product of the decomposition would tend to make the calorimeter line pressure continue to increase after the reaction period

instead of again reaching a constant value. A temperature equilibrium would not again be established as is ordinarily the case. In experiments C and D thermocouple readings were taken for a period of 60-80 minutes after the breaking of the bulb to check the possibility of amide formation. However, in both cases an equilibrium was established and there was no indication of any reaction taking place. The solution used in experiment D was also maintained for 44 hours with no visible sign of the amide being found at the end of that time. Therefore, on the basis of the above results, it seemed logical to rule out the possibility of amide formation as the cause of any experimental discrepancies.

The possibility of an inherent error in the experimental technique or apparatus remained as one of the most evident sources of error. To check both the technique and the apparatus a determination was made of the heat of solution of ammonium bromide in liquid ammonia. The results obtained are summarized in Table 32. The resulting heat of solution of -9350 calories agreed very closely with the value of 9410 calories obtained previously with this calorimeter. Schmidt had obtained a value of-9750 calories for the heat of solution of ammonium bromide, but this disagreement was probably due to the differences in the calorimetric apparatus used. Since the determination did check work previously conducted with this calorimeter, and since the variance with Schmidt's value was within reason, the possibility of an inherent error was dismissed.

Work on the solutions of the alkali metals in liquid ammonia indicated that it was more difficult to reproduce values for the heats of solution than for the heats of reaction with the ammonium ion. This is understandable when one considers that a heat of reaction determination would not be affected by light absorption. It was decided, therefore, in in view of the unsuccessful attempts to reproduce the heat of solution values, to perform measurements of the heat of reaction of calcium with the ammonium ion and to observe whether the discrepancies noted previously would be eliminated.

In measuring the heat of reaction of the alkali metals with the ammonium ion it had been found necessary to use some means of controlling the very rapid reaction rate. This had been accomplished by wrapping the sample bulb with a platinum wire gauze. A number of enlarged holes in the gauze regulated the rate at which the hydrogen produced during the reaction was evolved, thereby controlling the reaction rate.

Experiments 1 and 2 were performed with a platinum wire gauze wrapped tightly around the bulb. However the reaction between calcium and the ammonium ion is much slower than that with the alkali metals. At the conclusion of both experiments it was observed that a blue solution still was trapped under the wire gauze. This indicated that the gauze had prevented the calcium from reacting completely. The values of -75,700 calories and -84,500 calories obtained for experiments 1 and 2 respectively were widely separated and

served to strengthen the belief in the uselessness of the platinum gauze for calcium determinations. Therefore, in all subsequent experiments the wire gauze was not used.

The results of experiments 3 and 4 (Table 34) indicated no better agreement than in the heat of solution determinations. It was now evident that the source of error was one that was equally present in both the heat of solution and the heat of reaction measurements.

The calcium metal, from which all samples were made, had been specially prepared for this research, and the spectrographic analysis indicated only 800 parts per million of impurities to be present. Till this time, the purity of the calcium had not been questioned, but as a logical possibility it was decided to check the purity of the samples used. This could best be done by analyzing the contents of the calorimeter after a determination had been made. In this manner the actual amount of calcium participating in the reaction could be calculated and a correction made to the heat effect measured.

Experiments 4 and 5 yielded values of -87,700 calories and -101,800 calories respectively. However upon analysis of the calorimeter contents and correction of the experimental data the values of experiments 4 and 5 were -104,500 and -108,400 calories respectively. That the values now agreed within 4% indicated that the difficulty involved in all previous measurements made in this research was the impurity

of the calcium samples.

In correcting the experimental data for the actual amount of calcium taking part in the reaction it was assumed that all the impurity was in the form of calcium oxide, and that the heat of reaction of calcium oxide with ammonium ion in liquid ammonia was 30,000 calories(the basis for this assumption has been discussed previously). A detailed analysis to determine the extent of the impurities present and the heat effect involved in the reaction of each was deemed unwise for there would always be the uncertainty concerning the heat contents of the impurities as they exist mixed in the sample. Considering the assumptions made, an agreement of 4% in the experimental results of the heat of reaction determinations was as good as could be expected.

In view of the new findings redeterminations of the heat of solution of calcium in liquid ammonia were made in experiments F and G. The results obtained were corrected by a factor determined from the anlysis of the calorimeter to yield values of -22,800 calories at 1660 moles ammonia/gram-atom calcium and -21,900 calories at 1470 moles ammonia/gram-atom calcium respectively.

In correcting the heat of solution determinations it was assumed that the impurity consisted solely of calcium oxide, and that the calcium oxide was insoluble in liquid ammonia. This latter assumption was checked experimentally, and it was found that 2 milligrams of calcium oxide were

insoluble in approximately 210 grams of liquid ammonia.

The corrected values obtained for experiments F and G agreed within four percent. Again the uncertainty introduced by impurities was probably the source of error.

Though the discrepancies within the data obtained in this research had been explained, there still existed the disagreement with Schmidt. It was now attempted to explain this disagreement on the basis of Schmidt having made determinations with impure calcium.

The report of Schmidt's work gave ~~an~~ no analysis of the metal used other than to state that it was better than 99.5% calcium. When one considers the difficulty incurred in this research with specially prepared metal analyzed at better than 99.9% calcium, it seems logical to conclude that the metal used by Schmidt was also impure to some extent. If that had been the case, the value obtained by Schmidt would be lower than the true heat of solution. The fact that his values were less than half the corrected values obtained in this research served to strengthen the viewpoint taken concerning the calcium metal used in his measurements.

Seeking for some means by which a correction could be applied to Schmidt's data, it was decided to analyze a sample of commercial calcium probably of a nature similar to that used by Schmidt. The results obtained in a manner already described showed the sample to be 83.1% calcium. This corresponded to 40.5% of calcium actually present as calcium

metal. Assuming the remaining 59.5% to be calcium oxide, a correction was applied to the Schmidt data in the same manner that it had been applied to the results of this research. Table 33 shows both the original and the corrected Schmidt results. Where originally Schmidt obtained a value of -10,780 calories at 366 moles ammonia/gram-atom calcium, the correction produced a value of -25,900 calories at 616 moles ammonia/ gram-atom calcium. Similarly values of -24,900 calories and -24,100 calories at 696 and 900 moles ammonia/gram-atom calcium respectively were produced by a correction factor. These values were at least in the same range as those determined in this research.

In the above work it was assumed that Schmidt's calcium was identical with the commercial calcium analyzed. Though this was probably not the case, in view of the results obtained by applying this correction factor it seems logical to conclude that the metal used by Schmidt was at least of the same approximate purity as the commercial metal analyzed.

The heat of solution values obtained both by Schmidt and in this research are plotted in Figure 16. Points F' and G' are the corrected values of experiments F and G; S denotes Schmidt's corrected values. Interpretation of the results is difficult when one considers that no correction was applied in experiments A through E. Since the impurities were not uniformly distributed throughout the metal, it was not possible to make an analysis of the metal and thus determine a constant

correction factor. However, on consideration of the data, it is possible to assume that though sample D and E were impure to some extent, they were purer than sample C. The calcium samples used in experiments A and B also were probably impure. Therefore it is reasonable to assume that the values of A through E would at least be somewhat larger and at a somewhat greater dilution.

The exact curve that could eventually be drawn showing the variation of the heat of solution of calcium with concentration can therefore only be estimated, but it appears evident that a constant value corresponding to a heat effect at infinite dilution is approached at points F' and G'. Therefore the average of values F' and G' may be taken as ΔH_1, the heat of solution at infinite dilution.

Using the value of the heat of solution at infinite dilution, ΔH_1, and the value of the heat of reaction of calcium with the ammonium ion, ΔH_2, it was possible to obtain ΔH_3, the heat effect associated with the reduction of the ammonium ion by the solvated electron ($\Delta H_3 = \Delta H_2 - \Delta H_1$). Taking $\Delta H_2 = -106{,}500$ calories (the average of experiments 4 and 5) and $\Delta H_1 = -22{,}400$ calories (the average of values F' and G'), ΔH_3 was found to be equal to -84,100 calories. The result obtained agreed only within four percent with the theoretically expected value of -80,600 calories for two electron ionization of calcium in liquid ammonia. Such an agreement is as good as can be expected when one considers

the assumptions made during this research. From this work, therefore, it may be concluded that there is two electron ionization of calcium in liquid ammonia, and that those studies to the contrary could stand reconsideration on the basis of probable impurities in the calcium used. It seems very likely that the apparent anomalous behavior, in regard to both the absorption spectrum and the magnetic susceptibility measurements, could be explained in such a manner.

It is evident that both ΔH_1 and ΔH_2 should be redetermined using pure calcium where the uncertainty due to impurities is completely removed. Corrections can be made, as in this research, but the lack of agreement within experimental error of even the corrected values indicates that the true extent of the error introduced by impurities remains unknown.

This research may now serve as a foundation for further thermochemical studies of the alkaline earth metal solutions of liquid ammonia.

TABLE 33

The heats of solution of calcium obtained by Schmidt

	Sample wt.	Moles NH_3 /gram-atom calcium	Heat Effect	Heat of solution/ gram-atom
	0.1907 g	366.0	46.47 cal.	-9,764 cal.
	0.2470	282.0	62.36	-10,116
	0.2779	251.0	74.77	-10,780

Schmidt's values corrected on basis of analysis of commercial calcium (40.5% calcium metal, 59.5% calcium oxide)

	Sample wt.	Moles NH_3 /gram-atom calcium	Heat Effect	Heat of solution/ gram-atom
	0.0772 g	900	46.47	-24,100
	0.1000	696	62.36	-24,900
	0.1126	616	74.77	-25,900

The heat of solution values obtained in this research

Exp.	Sample wt.	Moles NH_3 /gram-atom calcium	Heat Effect	Heat of solution/ gram-atom
A	0.4025	760	238.1	-23,800
B	0.4248	615	283.5	-26,800
C	0.2139	1215	110.5	-20,400
D	0.1759	1390	101.1	-23,000
E	0.1998	1430	114.0	-22,800
F	0.1814	1530	89.7	-19,900
F'	0.1579	1660	89.7	-22,800
G	0.1945	1340	96.6	-19,900
G'	0.1774	1470	96.6	-21,900

The average of the corrected values of experiments F and G (F' and G')

$$\Delta H_1 = -22{,}400 \text{ calories}$$

TABLE 34
THE RESULTS OF THE HEAT OF REACTION DETERMINATIONS

Exp.	Sample wt.	Wt. Ammonia	Heat of Reaction/gram-atom calcium
1.	0.0421 g	116.45 g	-75,700 cal.
2	0.0400	115.68	-84,600
3	0.0380	116.73	-94,000
4	0.0376	116.64	-87,700
corr.	0.0305		-105,500
5	0.0396	116.82	-101,900
corr.	0.0368		-108,400

The average heat of reaction per gram-atom from the corrected values of experiments 4 and 5 is:

$$\Delta H_2 = -106,500 \text{ calories}$$

The value of ΔH_3 is

$$\Delta H_3 = \Delta H_2 - \Delta H_1 = -106,500 - (-22,400) = -84,100 \text{ cal.}$$

The theoretical value of ΔH_3 based on the alkali metal work is

$$\Delta H_3 = 2 \text{ x} -40,300 = -80,600 \text{ cal.}$$

VI. APPENDIX

A. Calibration of the Copper-Constantan Thermocouple TC-2

The copper - constantan thermocouple used in this research was calibrated at the sublimation point of solid CO_2 and the melting point of mercury. The experimental procedure involved and the method of preparing the thermocouple calibration table are described in the thesis of R. Maybury [9].

Though three methods for establishing a calibration table were presented by R. Maybury, only method (3) was used in this research. This procedure involved the use of equation (10) arrived at from a theoretical consideration of

$$(10)\quad e = at \pm bt^2$$

thermocouples. Substituting for t the values T_{CO_2} and T_{Hg} (in degrees centigrade) and for e the corresponding EMF's (in microvolts), two simultaneous equations were obtained. Solving these equations yielded the following values of the constants a and b:

$$a = -38.58$$
$$b = -0.05006$$

These values were inserted in equation (10) yielding equation (11).

$$(11)\quad e = -38.58t - 0.05006t^2$$

The following calibration table was set up using equation (11).

TABLE 35
CALIBRATION TABLE FOR THERMOCOUPLE TC-2

t(°C)	E_{TC-2}(μv.)	dE/dT (uv/°C)
-28	1040.99	
		(-29 °C) 35.68
-30	1112.35	
		(-31 °C) 35.48
-32	1183.30	
		35.33
-33	1218.63	
		35.22
-34	1253.85	
		35.13
-35	1288.98	
		35.02
-36	1324.00	
-38.78 (obs.)	1424.10	
-39	1428.48	
		34.62
-40	1463.10	

Temperatures corresponding to EMF's intermediate with those presented in this chart may be obtained by interpolation.

B. REDETERMINATION OF THE HEAT CAPACITY OF THE CALORIMETER USING A MORE ACCURATE METHOD[26]

The determination of the heat capacity involved duplicating the conditions that existed during an actual heat of reaction measurement. The reaction was simulated by introducing a known quantity of heat into the calorimeter at the same time that a previously determined volume of hydrogen gas was slowly bubbled through the ammonia. From the temperature change that occurred and the amount of ammonia vaporized the heat capacity of the calorimeter was calculated.

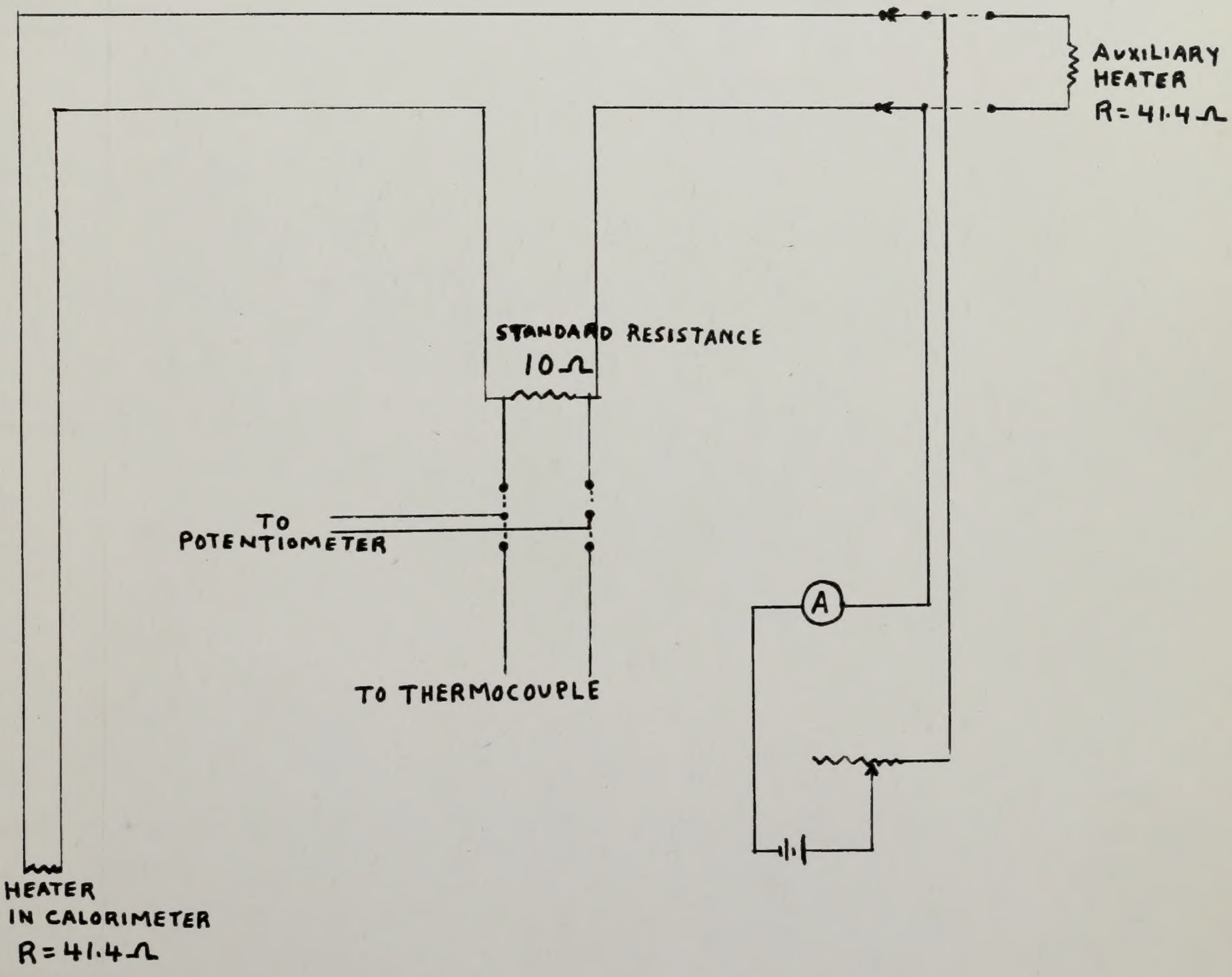
The experimental apparatus used in the heat capacity determination was the same as that used in the heat of reaction measurements with some slight modification. The calorimeter head now held, in addition to the stirrer and thermocouple, a heater in place of the sample bulb rod and a piece of 3 mm. glass tubing which served as a gas inlet tube. This inlet was connected to a calibrated gas burette.

A schematic representation of the heater circuit is shown in Figure 17. The heater, made of manganin wire, had a resistance of 41.4 ohms; the two leads of #32 copper wire were 77 cm. in length and had a resistance of 0.84 ohms. The potentiometer readings were taken across a standard ten ohm resistance.

[26] The heat capacity of the calorimeter had previously been determined by R. Maybury in his thesis work.

FIGURE 17

HEATER CIRCUIT FOR HEAT CAPACITY DETERMINATION


AUXILIARY
HEATER
R=41.4Ω
STANDARD RESISTANCE
10Ω
TO
POTENTIOMETER
A
TO THERMOCOUPLE
HEATER
IN CALORIMETER
R=41.4Ω

A weighed amount of ammonia was distilled into the calorimeter filling it to about the same height as does the ammonia in an actual determination. When the calorimeter and its contents had attained an equilibrium state, the simulated reaction was begun. The heater circuit was closed and a measured volume of hydrogen gas (92.83 ml.) allowed to bubble slowly through the liquid ammonia. Both thermocouple and heater readings were taken with the potentiometer. By using a double pole knife switch it was possible to switch rapidly between the thermocouple and heater circuits. The batteries supplying the heater current had been allowed to discharge continuously through an auxiliary heater, of exactly the same resistance as the heater in the calorimeter, for 24 hours prior to the determination. This provided a steady current flow through the heater during the "reaction" and enabled one to make accurate potentiometric measurements of the heater voltage. The ammonia gas vaporized was collected in the gas-collecting system. When all the hydrogen had been introduced into the calorimeter, the heater was turned off. Temperature measurements were taken till an equilibrium condition had again been established. All necessary cathetometer readings were recorded.

The total energy input during the heating period was calculated using equation (12)

$$(12)\quad q = \frac{I^2RT}{4.183}$$

where q was the heat input in calories, I was the mean heater current in amperes, T was the time in minutes, and R was the resistance of the heater and of that length of the leads immersed in liquid ammonia. I was calculated from Ohm's Law using the mean heater voltage measured across the standard ten ohm resistance. The heat input due to the heating of the leads in the calorimeter (but not immersed in the liquid ammonia) was calculated as above with R being one-half the total resistance of both leads.

The total heat input (q) equals the heat effect due to the vaporization of ammonia (wt. ammonia vaporized x heat of vaporization per gram) plus the heat effect associated with the change in temperature of the calorimeter and its contents (ΔT x heat capacity of the system). Setting the heat capacity of the calorimeter equal to x, and the heat capacity of the system, excluding that of the calorimeter, equal to A equation (13) was obtained.

$$(13)\quad q = T(A - x) + (\text{wt. ammonia})(\text{Heat of vaporization per gram})$$

Since the quantities q, ΔT, A, the weight of ammonia vaporized, and the heat of vaporization could be determined from the experimental data, x, the heat capacity of the calorimeter, remained the only unknown quantity in the above equation. Therefore the known values were substituted in the equation, and the equation was solved for the heat capacity of the calorimeter.

A summary of the data and calculations for the heat capacity determination is presented in Table 36. A value of 20.3 calories was found to be the heat capacity at a liquid height of 150.2mm.

The heat capacity of the calorimeter has been found to vary in a linear manner with liquid height. By plotting the value obtained in this research and two values obtained at different liquid heights with this calorimeter, Figure 19 was drawn. All heat capacity values of the calorimeter used in this research were taken from this plot.

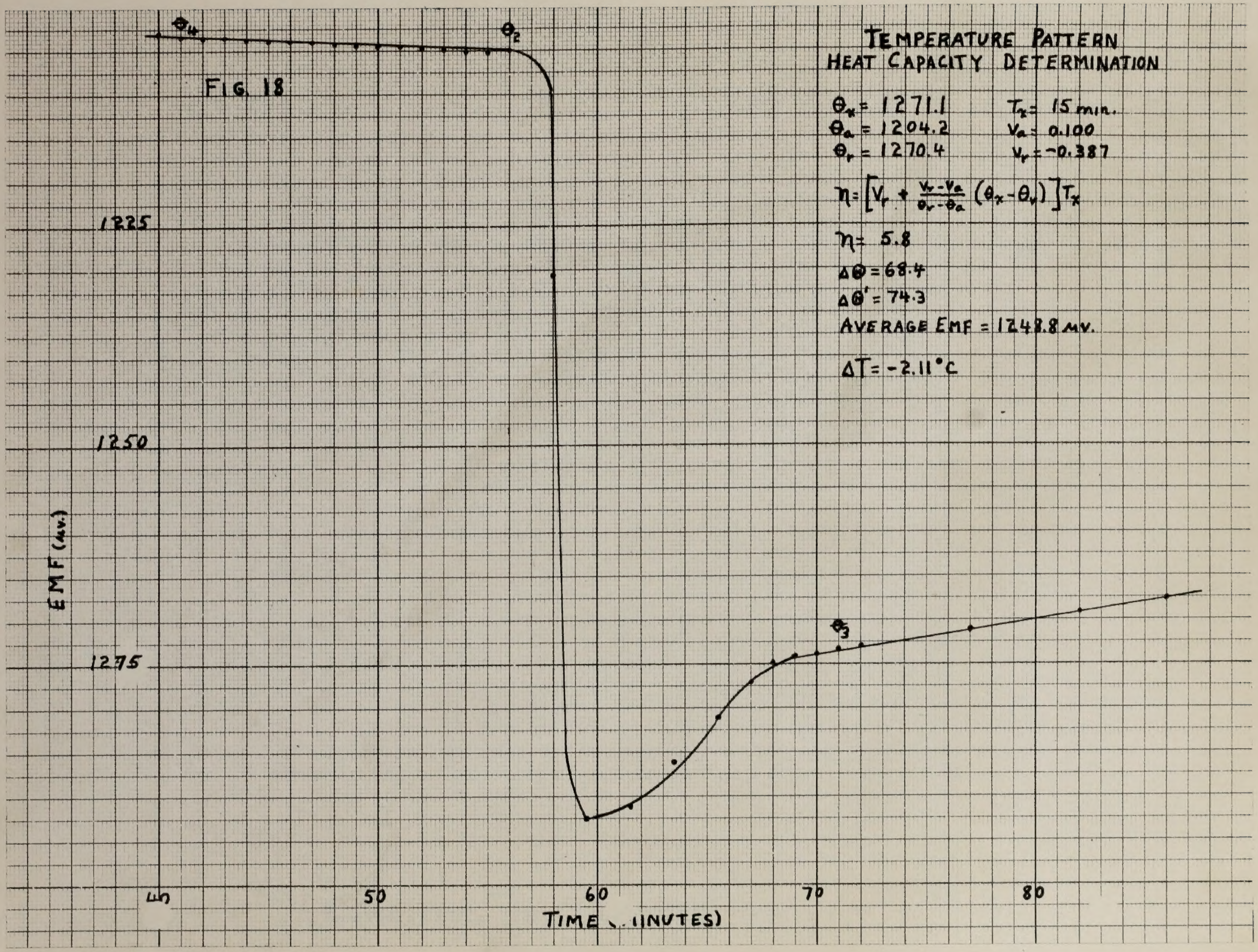


FIG. 18

TEMPERATURE PATTERN
HEAT CAPACITY DETERMINATION

$\theta_x = 1271.1$ $T_x = 15$ min.

$\theta_a = 1204.2$ $V_a = 0.100$

$\theta_r = 1270.4$ $V_r = -0.387$

$$\eta = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a}(\theta_x - \theta_r)\right]T_x$$

$\eta = 5.8$

$\Delta\theta = 68.4$

$\Delta\theta' = 74.3$

AVERAGE EMF = 1248.8 MV.

$\Delta T = -2.11$°C

FIG. 19

HEAT CAPACITY OF CALORIMETER

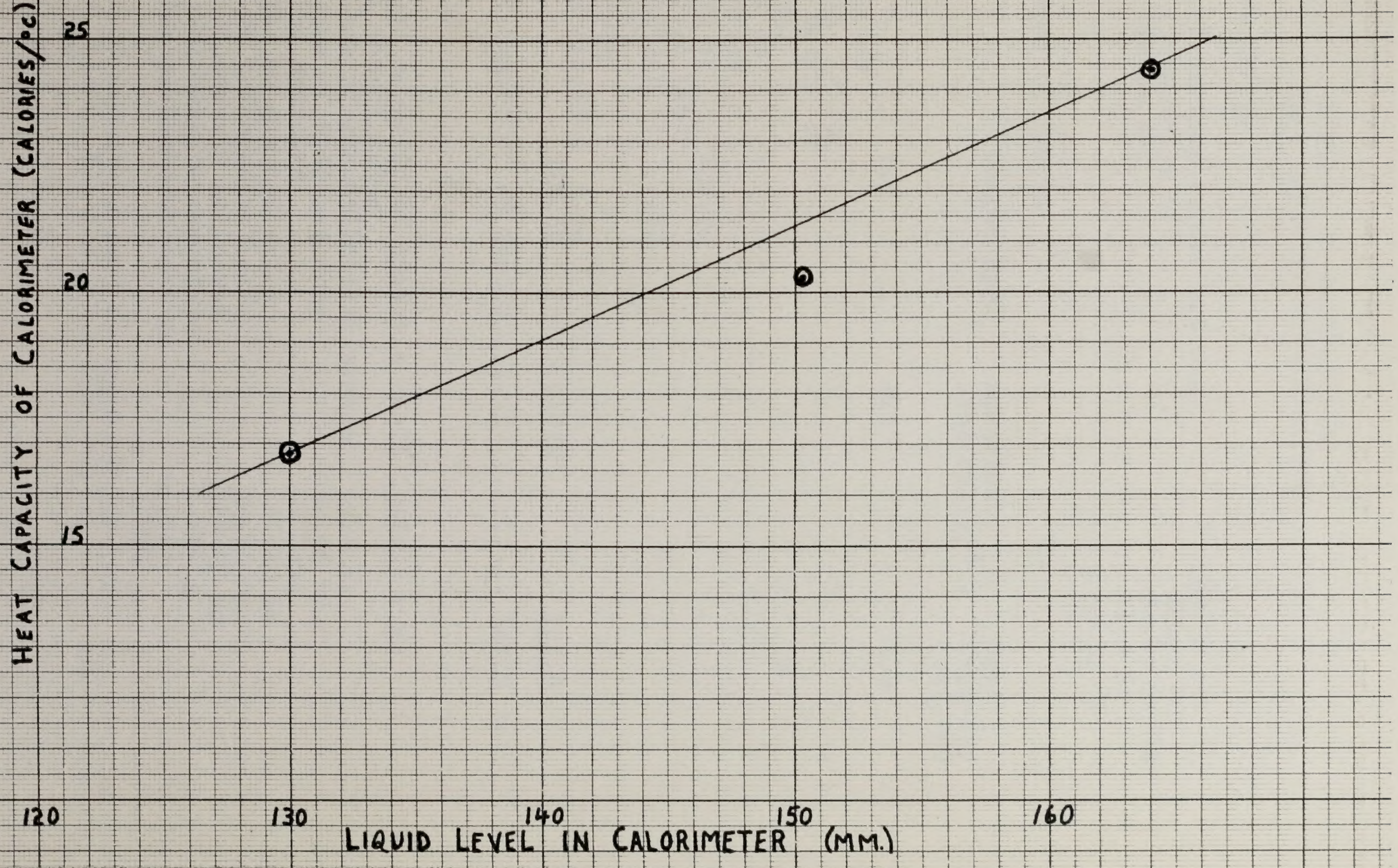


TABLE 36 SUMMARY OF CALCULATIONS
HEAT CAPACITY DETERMINATION

A. Temperature Change

Average E (from temperature pattern)	1248.8 uv.
Average T (from Table 35)	-33.86 °C
dE/dT (Table 35)	-35.18 uv/°C
ΔE (ΔⒽ)	74.3 uv
ΔT	-2.11 °C

B. Heat Capacity of System

Item	Weight (g)	Specific Heat(cal/g/°C)	Heat Capacity (cal/°C)
1. Glass	9.3	0.2	1.9
2. Calorimeter (from fig. 19 for liquid height of 150.2 mm)			x
3. Ammonia in calorimeter			
weighed in	122.01		
vaporized prior to reaction	1.49		
½ amount vaporized during reaction	0.66		
	119.86	1.065	127.6

Total Heat Capacity of System .... 129.5 x

C. Heat Effect

1. ΔT x Heat capacity of system = -2.11 (129.5 + x)
2. Heat of vaporization

a. Volume of gas-collecting system	6715 ml.
b. Volume of hydrogen used	92.83 ml.
c. Moles hydrogen	0.00494
d. Total mm gas collected	236.80 mm
e. Mm of hydrogen collected	13.95 mm
f. Mm of ammonia collected	222.85 mm
g. Wt. of ammonia vaporized	1.377 g
line pressure correction	-0.054
	1.323 g

h. Wt. of ammonia x Heat of vaporization per gram (Table 18) = 1.323 x 327.9 cal/g 433.8 cal.

3. Heat input

a. Resistance of heater 41.4 ohms

b. Resistance of leads immersed in ammonia	0.2 ohms
c. Length of time heater on	12 min.
d. Average heater voltage	1.27 volts
e. Average heater current	0.127 amps
f. Heat input due to heater and leads immersed in ammonia	115.9 cal.
g. Heat input due to leads in calorimeter but above liquid level	1.8 cal.
h Total heat input	117.7 cal.

4. Total Heat effect

$$117.7 = 433.8 - 2.11\,(129.5 + x)$$

5. Heat capacity of calorimeter at liquid height of 150.2 mm

$$x = 20.3 \text{ calories}$$

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VIII. ABSTRACT

The liquid ammonia solutions of the alkali metals have been found to possess certain anomalous properties which are generally similar for this series of metals. The similarity is most markedly demonstrated by conductivity and absorption spectra measurements.

Kraus proposed the following equilibria to explain the unique properties of these solutions:

$$M \rightleftarrows M^+ + e^- \qquad e^- + xNH_3 \rightleftarrows e^-_{(xNH_3)}$$

Recent magnetic studies have forced modification of the original Kraus theory but, aside from the positive ion, the theoretical nature of the solutions remains the same, namely the solvated electron.

Since the presence of the solvated electron has been confirmed experimentally, it may be expected that the properties of ammonia solutions dependent upon the solvated electron will be the same for all the alkali metals. Recent thermochemical studies showing all the alkali metal solutions to possess a similar heat of reaction with the ammonium ion in liquid ammonia has strengthened this view.

Extension of this concept of solutions to the alkaline earth metals would lead one to expect properties of a similar nature when compared on a proper concentration basis. This may be questioned, however, when one considers absorption spectrum studies and magnetic susceptibility measurements

made on solutions of the alkaline earth metals in liquid ammonia.

One electron ionization was suggested as a possible explanation of the abnormal molal susceptibility of calcium solutions. Density measurements indicated that such a situation probably exists in concentrated solutions.

The problem of one or two electron ionization was approached thermochemically in this research. The value for the heat of reaction of the solvated electron and the ammonium ion in the alkali metal solutions served as a basis for the comparison of calcium solutions.

Determination of the heat effect associated with the reaction between the solvated electron and the ammonium ion was made by combining the two easily measured heat effects (1) the heat of solution, ΔH_1, and (2) the heat of reaction with the ammonium ion, ΔH_2.

It was the purpose of this research to determine these heat effects calorimetrically, and by their combination to arrive at the heat effect, ΔH_3, associated with the reduction of the ammonium ion by the solvated electron.

ΔH_1 was found to equal -22,400 cal. ± 2%, and ΔH_2 was determined to be -106,500 cal. ± 2%. Using these two values ΔH_3 was found to be -84,100 cal. ± 2%. This was compared with the theoretically expected value of -80,600 cal. (2 x 40,300 cal.) for two electron ionization. Since the values of ΔH_1 and ΔH_2 had to be corrected for impurities in

the sample, the agreement of the ΔH_3 values was considered as good as could be expected. It was concluded, therefore, that there was two electron ionization of calcium in liquid ammonia.

The values of ΔH_1 did not agree with previous measurements of the heat of solution of calcium. The probability of impurities in the metal used in the earlier determinations was offered as an explanation of the discrepancy.

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